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General introduction

The majority of the convenience goods are based on plastics that are produced from fossil oil. Their convenient implementation makes them the perfect material for packaging and short life products. Due to their low density plastic trashes are all over the planet and accumulate because of a low degradability which became a serious source of pollution in the last decades. This, associated to the upcoming depletion of fossil oil in a near future created a need for bio-degradable (reducing pollution) and bio-based (independence from fossil oil) plastic substitutes.

Fragmenting polymers (oxo-fragmenting, bio-fragmenting) have first been designed in order to reduce the visual pollution, but this solution was rapidly criticized because of the dissemination of micro and nano-particles all over the biosphere that could not be recovered from the soil and water they were dispersed in. In the last decades, biodegradable polymers have become a reality with the industrial scaling up of PLA (polylacticacid) production which was furthermore bio-based. With help of the biotechnologies, other bio-based polymers were invented like PHA's (polyhydroxylalkanoates) for instance. These productions were dependent on crops and biotransformation, which took some time to become industry-viable, and by this time, other bio-degradable polymers like PBAT (polybutyleneadipate co terephthalate) were developed from fossil oil, which have rapidly been more easily available, with secured supply and easier processability. More recently, partially or totally bio-based replacement for classic plastics has also been designed with the idea of independence from fossil oil and production of durable material that would be easily recycled for example bio-PVC (polyvinylchloride), bio-PE (polyethylene) and PEF (polyethylenefuranoate, alternative to PET – polyethyleneterephthalate). This tendency considers that in some cases plastic re-use could be more eco-efficient than biodegradation. Finally, native polymers (i.e. polymers naturally occurring in nature) have gain interest especially starch that rapidly found industrial applications, purified or in whole plant version (for example Mater-bi, or the whole plant maize plastic alternative produced by Vegeplast in France). Proteins crops residues like sunflower are also close to find industrial application.

The possibility of finding natural thermoplastic polymers (if verified to be biodegradable) appeared a great opportunity for reducing pollution and fossil oil dependency… until the competition between food and convenient goods (plastic but also fuels) on the food-use was considered. One last possibility could be in the focus on agricultural wastes and non-edible parts of plants like straws and other residues that are mostly composed of ligno-cellulosic compounds.

Paper is a bio-based, bio-degradable material that is known for centuries and which matches most of the eco-requirements although the pollution of wastes due to cellulose extraction (pulping process) is disputable. A modern development of paper conducted to Zelfo, which was obtained upon a more advanced separation of cellulose fibers by Zellform GesmbH in the 1990's (Döpfner et al. 1997). Cohesion is obtained, like paper, by hydrogen bonding established when water evaporates. Micro-fibrillation provides enhanced mechanical properties to Zelfo, but time and/or energy costly drying and consequent shrinkage of objects upon drying are important drawbacks that did not permit an industrialization, even after the glorious work of Omodo Gmbh in the 2000's that conducted to win the "Biomaterial of the year 2011" prize at the Nova institute international congress on bio-plastics (Cologne, Germany).

In 2007, the young company "The Green Factory" bought a license to Omodo with the idea of starting research collaboration in order to develop and possibly industrialize the Zelfo. Omodo and TGF became partner short after and worked together on the production of Zelfo using twin screw extruders for increased efficiency and lowered costs. Another partner was found with the LCA, which has been working for decades on the bio-refinery of agricultural wastes and other biomasses, and with some experience in the thermo-mechanical treatment and thermo-forming of lignocellulosic materials remaining after extractions of other interesting compounds. From this collaboration begun some first experiments and a patent

(WO2012069736, Rouilly et al. 2012) concerning was deposited before the beginning of this thesis in co-ownership between the INPT (National Polytechnic Institute from Toulouse) and The Green Factory. Short after this first collaboration was born this ANRT (French National Agency for promoting Research and Technology) PhD thesis: *Study of a thermo-compression-process for the molding of natural lignocellulosic materials without pretreatments or binders*. The idea was to study the possibilities of thermo-compression as a single step molding technique for the processing of lignocellulosic residues into simple, raw, yet valuable materials and possibly work towards the development of a new molding route for Zelfo. Meanwhile, an ANR (National research agency) project (HYPMOBB, High Pressure Molding of Biopolymers and Biomolecules) started in the laboratory which comprised a PhD thesis directed towards the study of the behavior of starch and cellulose under mechanical pressure (Jallabert 2014, PhD thesis).

Five chapters compose this PhD work thesis:

The first chapter contains a literature review over the thermo-compression molding of lignocellulosic materials which has been published recently (Pintiaux et al. 2015). The analysis of the literature permitted to consider the important parameters to analyze in the processing of plant materials by thermo-compression molding. Some inspiration was also taken for designing apparatus and techniques.

Chapter II presents a technological discussion around the "thermo-compressive molding". This thesis consisted in a lot of prototyping and technological research around the thermo-compression molding, and thus it is important for the reader to take note of this first part before getting to the results.

Although being the major constituent of plant, very few results existed on the processing of pure cellulose by thermo-compression in the literature. Chapter III is an extensive study of the thermo-compression of pure cellulose, chosen as a model polymer in the early stages of this thesis. The influence of the molding parameters have been examined separately, and results published in a first paper (Pintiaux et al. 2013). Based on these first results, following studies were run on the pressure response, water properties and the temperature / moisture couple which was identified as the most impacting parameter. In regard to the results obtained in the PhD thesis of Jallabert, hypotheses are drawn towards the explanation of a new kind of cohesion mechanism.

Chapter IV gathers results obtained towards the improvement of the water resistance of materials obtained by the thermo-compression of cellulose with fatty compounds added as hydrophobating agents. After a first mapping on the potential compounds, a deeper study was performed on a very specific case in order to investigate the actual grafting of one hydrophobic compound on cellulose during the thermo-compression process.

In chapter V, the influence of other compounds than cellulose on the properties of the resulted thermo-compressed specimens was studied, based on a mapping of several plant materials collected on other projects in the laboratory. Although encountering some technical troubles, statistical analyses permitted to draw some conclusions about the necessary features of plant materials for being molded into valuable materials using compaction molding and a methodology was investigated towards the production of these materials using transfer molding.

The references cited, materials and methods chapter and the tables of figures are presented at the end of this manuscript.

Abbreviations

σ_f: Flexural strength at break, bending strength at break (MPa)
σ_t: Tensile strength at break (MPa)
AIST: Aishi Institute of Science and Technology, host laboratory for the JSPS internship.
cont.: is used as an abbreviation for content, when needed
CEF: Cellulose elementary fiber
DMA: Dynamical Mechanical Analysis
DP: Degree of Polymerization
DS: Degree of Substitution
DSC: Differential scanning calorimetry
E_f: Flexural modulus, bending modulus (GPa)
E_t: Tensile modulus (GPa)
GR: Grafting Yield
IB: Internal bonding
LCA: Laboratory of Agroindustrial Chemistry, host laboratory
MC: Moisture Content
MFC: Microfibrillated cellulose
MOR: modulus of rupture, equivalent to bending strength at break.
MOE: modulus of elasticity, most of the time corresponds to the bending modulus
NFC: Nanofibrillated cellulose
OA: Octanoïc acid
OAn: Anhydride octanoïc
PC: Principal Component
PCA: Principal Components Analysis
RH: Relative Humidity
SG: Specific Gravity, also density (g/cm^{-3})
TGA: Thermo-gravimetric analysis
TGF: The Green Factory, financing company, changed name to Zelfo technology
TS: thickness swelling, percentage of thickness increase, measured on a 50 mm square sample after 24 hours dipped in 20°C water
WA: water absorption, percentage of mass increase during the TS test

I Literature review: binderless materials obtained by thermo-compressive processing of lignocellulosic fibers

Plants cell walls can be regarded as being high-end engineered nano-scale composites basically composed of cellulose, lignin, and hemicelluloses (Rose 2003). The supra-molecular organization in the plant cell wall provides fascinating unique mechanical properties (Niklas et al. 2006). Being the basic constituent of plants and because very few organisms can degrade it, cellulose is the most widely occurring polymer on planet earth. This polymer, made of ß-1-4 linked D-hydroxyglucopyranose, has an extraordinarily strong and rigid molecular design. The macroscopic Young's modulus of plant cellulose has been measured at 128 GPa (Page et al. 1971), which is higher than aluminum (70 GPa) or glass fibers (76 GPa) (Lo and Hoa 2006). The Young's modulus of the crystal of cellulose has been estimated to be 138 GPa (Sakurada et al. 1962). With low density and high mechanical performance, it provides amazing strength and growth possibilities to plants e.g. trees of 115 meters height (sequoia sempervirens, Redwood national park, California, USA) and 14.4 meters of diameter (taxodium mucronatum, Arbol del Tul, Oxaca, Mexico) can be found. Bamboo for example is a well-known strong and fast-growing plant widely used for small constructions in Asia. All civilizations have worked with wood or other plant materials to build tools, furniture, housing and many sorts of goods.

A comparison of mechanical properties of synthetic and natural fibers is provided in Table I - 1 (Eichhorn et al. 2001). It shows that plant fibers from diverse origins have various mechanical properties, and they can in some cases compete with glass fibers, if their relative densities are taken into consideration.

Table I - 1: Properties of different plant fibers and synthetic fibers, adapted from Eichhorn et al. (2001)

Fibre	Density (g.cm^{-3})	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (GPa)
Cotton	1.5-1.6	7-8	287-597	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Hemp	-	1.6	690	-
Ramie	-	3.6-3.8	400-938	61.4-128
Sisal	1.5	2-2.5	511-635	9.4-22
Coir	1.2	30	175	4-6
Viscose (cord)	-	11.4	593	11
Soft wood Kraft	1.5	-	1000	40
E-glass	2.5	2.5	2000-3500	70
S-glass	2.5	2.8	4570	86
Aramid (normal)	1.4	3.3-3.7	3000-3150	63-67
Carbon	1.4	1.4-1.8	4000	230-240

Furthermore, plant fibers are renewable, biodegradable, and safe for humans and the environment. Using natural fibers instead of petroleum-based material or highly consuming energy materials such as concrete or metal alloys is highly promising for reducing the greenhouse effect and drastic climate change as well as not contributing further to today's immense plastic waste environmental pollution (Lebreton et al. 2012).

Of course, interest in the use of natural fibers for materials has been motivated by raising environmental consciousness. Such interest is revealed by the number of scientific articles related to the introduction of plant fibers in composites using a classical thermoplastic matrix (e.g. PVC, PE), which could also be partially bio-based (biobased PE / PVC) to produce partially bio-based composites (Faruk et al. 2012), and also with a

biodegradable matrix to produce fully biodegradable composites (e.g. PLA, PBAT, PHA's) even on a nano-scale (Reddy et al. 2013).

Another option is the use of plant fibers in a natural bio-based and biodegradable matrix, e.g. starch or proteins to create a 100% bio-based and biodegradable composite product (Rouilly and Rigal 2002). The fact that every thermoplastic biopolymer comes from edible resources for humans has raised ethical problems because of the possible land-use competition between food and convenience goods. Therefore, 100% lignocellulosic fibers materials have to be designed based on agricultural wastes such as cereals straws, oilseed cakes, etc.

Wood is also the input material of another huge industry: paper and its derivatives, wherein water suspensions of wood fibers (pulps) are processed by squeezing and drying. These "wet processes" will not be reviewed here. Neither will the solubilization processes be considered (e.g. Lyocell, Carbamate), on which a review was recently published (Fink et al. 2014). Pharmaceutical tablets that contain cellulose or starch as excipient will also be omitted because of the differences of process (ram compression, cold processing to prevent damage to the active components, and size of the molded objects).

Wood processing includes many technologies to cut, machine, deform, and assemble pieces of wood without any additives, which produce eco-friendly materials, until the wastes (saw dust, useless cuts, etc.) are considered. Saw dust and wood particles used to be mainly burnt and composted (both disposal techniques released CO2 to the atmosphere), but today they more and more enter in processes to be assembled with binders or polymers to form boards or more recently wood-polymer composites (WPC). Thermoset resins are based on fossil resources, and most of them are formaldehyde-based, resulting in emissions of formaldehyde from the final products with potential harm to customers and the environment (Tunga Salthammer et al. 2010). The replacement of resins is also considered for economic reasons because of the increasing part of resins in the cost of particleboard production (Hashim et al. 2010), and even the recycling of the formaldehyde from waste wood-based panels has been considered .

The situation just described provides reasons for the recent spike in researchers' interest in pursuing studies on the processing of various plant materials into boards without the use of additives, binders, resins, or chemical modifications, which is precisely the aim of this literature review. This work will then focus on the thermo-compressive processing of non-modified plant fibers without additives. Because of the interaction of parameters one to the others and with water (which plays a major role) and because of the high diversity of compositions and complicated structures of plant fibers, attention has been placed on isolating parameters and effects, and precise research facts have been reported here in order to highlight past achievements and future directions.

Definitions

In the wood-based panel industry, particleboard (PB) products mainly are made from wood particles (chips) recycled from wastes that are glued together with petroleum-based binders. Oriented strand boards (OSB) are quite similar but the wood particles that compose them are bigger with a particular flat geometry, i.e. like flakes. Fiberboards (FB) on the other hand, are made from wood fibers, thinner elements that have been first separated in a refiner. Finally, hardboards (HB) are produced from steam-exploded wood particles and, if they are subjected to a wet process (Masonite) they do not require binders.

While the materials and processing conditions used in present-day production of particleboard, strand board, and fibreboard products can provide a practical point of focus for this review, some of the best evidence regarding the mechanisms underlying the successful preparation of binderless board products can be found outside of the scope of conventional wood-based panel manufacturing. Indeed, most of the research works gathered during the preparation of this review did not employ wood and had experimental conditions that would

not fit the wood-based panels standards (e.g. higher density, longer pressing time, and higher temperature). This article focus on collecting the technological possibilities to produce self-bonded lignocellulosic materials and explanations about the self-bonding mechanisms, for which it is important to take into consideration all types of boards and confront the results (e.g. differences and commonality between steam pretreatment, steam injection, and no-steam processing). The mechanisms of cohesion in the different types of binderless boards are assumed to be comparable; thus, when possible, the term "binderless particleboards" (no refining) have been used as well as "binderless fiberboard" when a refining step was present. If reported panels do not fit in a category, or when the elements concern all types of boards, the generic term "boards" has been used.

In addition, a distinction will be made between steam-pretreated binderless boards, which in most cases are indeed in the fiberboards type, and those which are not. Most of the examples that enter the category of "non-steamed" boards would be in the particleboards type.

Usually boards are "pressed" (at low pressure) and 3D objects are "molded" (at higher pressure) but, because the mechanisms of cohesion are discussed against pressure and since selfbonding of "pressed" and "molded" materials relies on the same physico-chemical phenomena, the term "molded" will thus be used for comparison when needed.

Delamination refers to the creation of cracks in compressed materials due to excessive steam production within the specimen. Delamination most probably occurs at high temperature and moisture content (MC) when pressure is released within the specimens. An extreme case of delamination can make the materials explode upon depressurization of a mold. Delamination is a casually identified limit in binderless boards' production and is further discussed in the paper.

History of binderless compression-molded plant materials

Binderless boards were born with the Masonite® process (Mason 1928). William H. Mason invented a process for producing wood fibers hardboards, using a steam pretreatment step. The chemo-mechanical action inherent in the pretreatment released components from the fibers on their surface to form an in situ glue. For historical reasons, because of the close interaction of plant fibers and moisture and the very similar chemistry changes occurring upon steam treatment and during hot pressing, steam processing will be considered in this review.

Later, a patent of Runkel and Jost (1956) described a process called Thermodyn for producing binderless boards from plant material without requiring steam. The inventors described two stages in the process: during the first step, degradation gases are produced from plant materials under heat and pressure, and these serve as hydrolyzing agents to produce binders from the plant materials. This first step is very much like Mason's steam treatment, although it occurs in the mold. In a second step that could be separated, the material is molded into the desired shape. Some details are missing in the patent. For example no problems are mentioned concerning steam delamination, rheological behaviour, mechanical properties, or water resistance. Runkel and Jost reported "physical, colloidal, chemical changes of the cell wall components, leading to some sort of thermoplasticity of the material occurring under compression, heat, and in the presence of a little moisture", and there is no doubt that these phenomena are keys to understand the moldability of 100% natural fibers. The interest in this process was probably not sufficient in comparison to petroleum-based thermoplastics so unfortunately the Thermodyn process did not leave behind an imperishable memory.

More recently, Mobarak et al. (1982) published what is today' oldest available academic paper on binderless boards made from unmodified natural plant materials (Mobarak et al. 1982). The paper starts with a very nice overview on the older scientific

works that are in Russian and German, and most of them not easily available. They haven't been taken into consideration for this review.

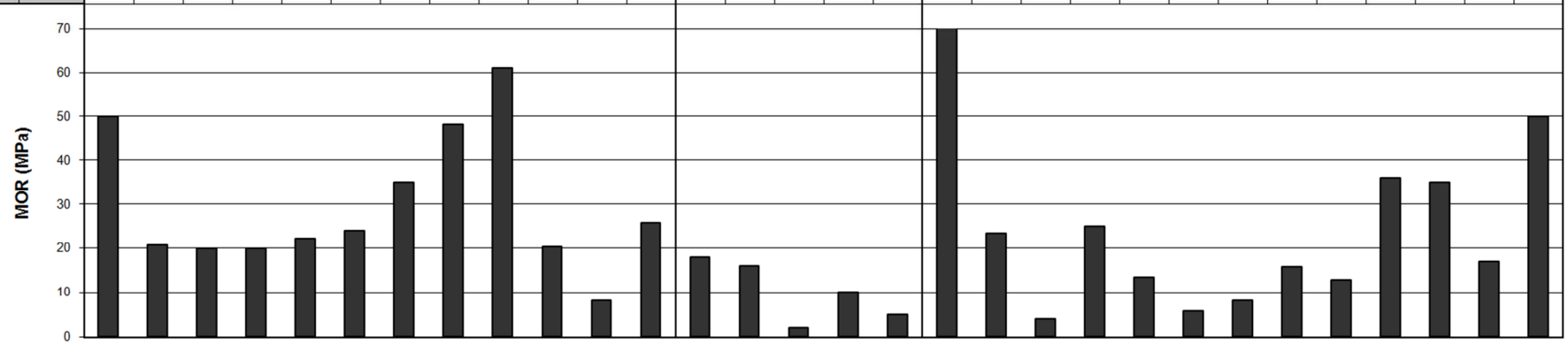
I.1 An overview of the mechanical properties and water resistance of self-bonded materials obtained by thermo-compressive processing of plant fibers

I.1.A Mechanical properties of self-bonded thermo-compressed plant materials

The concept behind binderless molded objects probably appeared with the idea of avoiding the use of environmentally harmful binders. It is reasonable to assume that at first, available production tools (pressing machines) were used; therefore, a first "boards" category can be made, for which the process uses available and relatively low pressure. Researchers working on binderless boards have the standard wood-based panels' properties as reference and not the processing conditions. Most of the time, the idea of binderless boards research is to reach the industrial wood–based panels properties (with adhesive) without using binders. However, the higher temperatures and much longer times required to meet quality standards may fall outside of the norms for commercial production.

Table I - 2: Summary table of mechanical performances of binderless boards and compared properties obtained by steam pretreatment, steam injection pressing and without treatment*

		Steam pretreated materials												Steam injection					No steam													
Reference		Howard and Sandborn 1937	Suchsland *et al.* 1987	Suzuki *et al.* 1998	Suzuki *et al.* 1998	Laemsak and Okuma 2000	Anglès *et al.* 1999	Anglès *et al.* 2001	Velasquez *et al.* 2003	Salvado *et al.* 2003	Gao *et al.* 2011	Nachari *et al.* 2013	Saari *et al.* 2014	Xu *et al.* 2006	Xu *et al.* 2003	Xu *et al.* 2004	Widyorini *et al.* 2005b	Widyorini *et al.* 2005b	Mobarak *et al.* 1982	Shen 1986	Hashim *et al.* 2010	Hashim *et al.* 2010	Hashim *et al.* 2011a	Hashim *et al.* 2011b	Nachari *et al.* 2013	Boon *et al.* 2013	Saadaoui *et al.* 2013	Okuda and Sato 2004	Okuda and Sato 2006	Nonaka *et al.* 2013	van Dam *et al.* 2004b
Plant material		Wood	Green hardwood	Oil palm tree fronds	Oil palm tree fronds	Oil palm tree fronds	Spruce and pine residues	Spruce and pine residues	*Miscanthus sinensis*	*Miscanthus sinensis*	Black spruce bark	Oil palm trunk	Oil palm trunk strands	Kenaf core	Kenaf core	Kenaf core	Sugar bagasse pith	Sugar bagasse rind	Bagasse pith	Bagasse	Oil palm trunk fines	Oil palm trunk strands	Oil palm trunk core	Oil palm trunk	Oil palm trunk	Oil palm trunk	Palm date tree fibrillum	Kenaf core	Kenaf core	Bagasse	Coconut husk
Density (g.cm^{-3})		1.44	1*	1.2	1.2	1.2	1	1.07	1.18	1.27	0.98	0.8*	0,8*	0.5*	0.7	0.25	0.75	0.75	1.35	0.75	0.8*	0.8*	0.8*	0.8*	0.8*	0.62	0.97	1*	0.7	0.75	1.35
Properties (MPa)	IB	-	2.5	1.85	0.59	1.8	1.8	1,8	1.2	3.76	1.77	0.49	1.4	0.55	0.6	0.15	0.2	0.2	-	0.74	0.47	0.93	0.71	0.93	0.49	0.6	0.02	5.7	4.9	1.2	-
	MOR	50	20.7	20	20	22.4	24	35	48.2	61	20.3	8.18	25.8	18	16	2	10	5	130	23.5	3.99	25	13.4	5.73	8.18	15.8	12.9	36.1	35	17	50
	MOE	-	3709	4227	7610	-	4000	7500	6050	6600	2360	-	-	2300	3000	500	1500	1000	-	5240	-	-	-	-	-	-	1257	5500	5500	3500	5000



An asterix (*) in the density line means that target density is reported and not the actual density measured.

Boards-type, low pressure molding

Mechanical properties of boards are commonly expressed with the use of three variables, the modulus of rupture (MOR), the modulus of elasticity (MOE), and internal bond (IB). Somehow, these three parameters are correlated. Plant materials do not produce rubber-like materials (high MOR and low MOE), and the IB is also somehow correlated with the bending properties. As the most common usage of boards (e.g. flooring, furniture) relies on strength of the boards, the MOR is the first criterion.

Table I - 2 presents a quick comparison of the performances of steam-pretreated, steam-injection pressed, and non-treated-materials binderless boards. All of the values reported in this table come from the highest MOR obtained by researchers, with the MOE and IB reported on the same specimen. It can be observed that steam pretreatment always produces relatively strong products with decent MOR, whereas direct hot pressing without any treatment of the starting materials can produce either low or high mechanical properties. This basically means that the molding of natural fibers without any treatment is more sensitive to the nature of starting material. Some materials would be suitable for direct molding and do not need steam treatment, whereas some others would require it.

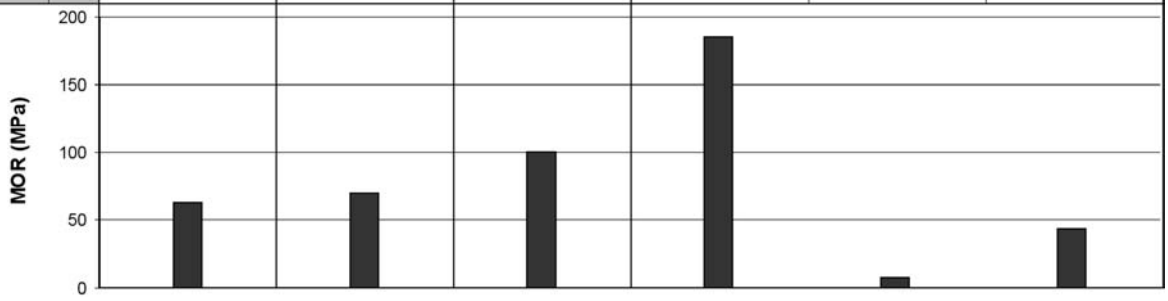
High pressure, plastic-substitute type, cellulose processing

Research involving new materials as well as the need for understanding the chemical changes and processing possibilities of lignocellulosic materials have led some researchers to work at higher pressure. In this review, the "high pressure" range would start at around 30 MPa. But more than the value, "high pressure" is defined by the intent from the authors to mold products towards the creation of new materials, with higher density and properties, usually at a smaller scale. This would not be with the idea of producing boards, but more likely plastic materials, which potentially can be three-dimensional, extrusion tests, or transfer molding. Raw lignocellulosic materials have been processed at high pressure (Miki et al. 2003), sometimes together with steam (T. Miki et al. 2007; Takahashi et al. 2010), and pure cellulose compression molding was also studied (Nilsson et al. 2010; Rampinelli et al. 2010; Zhang et al. 2012; Pintiaux et al. 2013; Privas et al. 2013). The “ECAP” process (Equal Channel Angular Pressing) of Zhang et al. (2012) comes from metallurgy and involves the material being subjected to high shear stress; this approach is comparable to transfer molding as experimented by Miki et al. (Yamashita et al. 2007) yet quite different from compaction molding (low and high pressure), wherein shear is limited. The influence of shear is an interesting parameter, however not very much described in molding, but well known in the wood welding process from the group of Pizzi et al. (Gfeller et al. 2003).

Obviously, as can be seen in Table I - 3, high pressure can result in considerably higher MOR than low-pressure molding, and the resulting densities fall in a narrow range of 1.4 to 1.5 g/cm^3. Results obtained on pure cellulose are quite disappointing compared to lignocellulosic materials unless the material has been refined (micro-fibrillation).

Table I - 3: Summary table of mechanical performances of high pressure molding experiments for producing self-bonded plant materials

		Steam pretreated materials	Steam atmosphere pressing	Non steam treated			
Reference		Takahashi *et al.* 2010	Miki *et al.* 2008	Miki *et al.* 2003	Rampinelli and Di Landro 2010	Zhang *et al.* 2013	Pintiaux *et al.* 2013
Plant material		Beech wood	Cypress and cedar wood (1:1)	Cedar wood	Micro fibrillated cellulose (*i.e.* refined)	Coton linters microcristalline cellulose	α-cellulose
Pressure (MPa)		30	36.5	178	120	-	267
Density (g.cm^{-3})		1.45	1.4	1.4	-	-	1.51
Properties (MPa)	MOR	63	70	100	185	7.6	43.2
	MOE	11000	8000	-	-	3215	7170



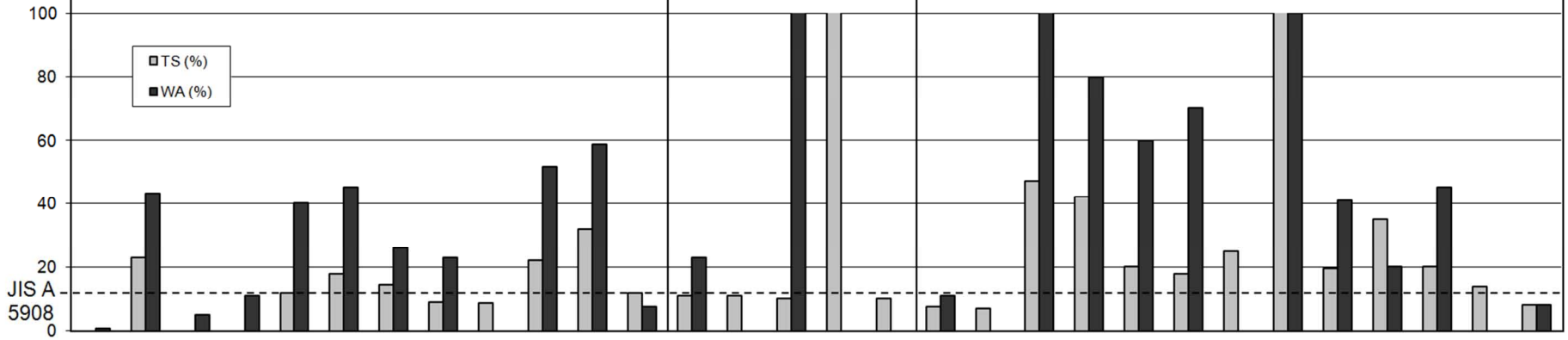
I.1.B Water resistance of self-bonded thermo-compressed plant materials

Water resistance is classically evaluated by measuring the water absorption and thickness swelling of 5x5cm specimen samples, which is convenient for comparisons. Different standards are to be found in different parts of the world. The European system (EN standards), for example, is quite complicated. TS requirements are specific depending on the type of panel (particleboards P1 to P7, EN 309 – medium density fiberboard, EN 622-5 – oriented strand board types 1 to 4, EN 300). Particleboards of type 3 to 7 have requirements of TS depending on specifications (humid environment or not). Medium density fiberboard and oriented strand board also have increasing specification of resistance against water, and all the values required by the standards vary as a function of the boards' thickness. Japanese standards, however, are much more convenient, requiring that any type of boards should have a TS lower than 12% (according to JIS A 5908 2003). The explanation for application of such a broad standard probably arises from the very humid Japanese weather. The 12% maximum TS from the Japanese standards is found as a reference in many publications and has been reported here in Table I - 4. In this table, it can be observed that binderless boards have difficulties to achieve water resistances good enough to pass the standards. The use of steam, however, appears to significantly increase the water resistance.

Okuda and Sato (2004) reported that the mechanical properties of their binderless boards made from kenaf core became reduced to (only) 1/3 of their dry value when placed in wet conditions (Figure I - 1) for specimens in the high range of IB. Another promising value of 87% was reported upon high-temperature molding of bagasse (Nonaka et al. 2013). Mechanical properties in the wet state are very rarely reported, and these two examples are actually excellent values; sometimes, water resistance tests (TS / WA) are not even reported because the specimens swelled and broke down in water.

Table I - 4: Summary table of water resistances of self-bonded thermo-compressed plant materials and comparison between steam pretreatement, steam injection and without steam*

	Steam pretreatment												Steam injection pressing					Without steam												
Reference	Howard and Sandborn 1937	Suchsland *et al.* 1987	Suzuki *et al.* 1998	Laemsak and Okuma 2000	Anglès *et al.* 1999	Anglès *et al.* 2001	Velasquez *et al.* 2003	Salvado *et al.* 2003	Gao *et al.* 2011	Nadhari *et al.* 2013	Saari *et al.* 2014	Takahashi *et al.* 2010	Xu *et al.* 2006	Xu *et al.* 2003	Xu *et al.* 2004	Widyorini *et al.* 2005b	Widyorini *et al.* 2005b	Mobarak *et al.* 1982	Shen 1986	Hashim *et al.* 2010	Hashim *et al.* 2010	Hashim *et al.* 2011a	Hashim *et al.* 2011b	Boon *et al.* 2013	Saadaoui *et al.* 2013	Okuda and Sato 2004	Okuda and Sato 2006	Ando and Sato 2010	Nonaka *et al.* 2013	van Dam *et al.* 2004b
Starting material	Fine materials after masonite gun	Hardwood	Oil palm tree fronds	Oil palm tree fronds	Softwood (Spruce and Pine) residues	Softwood (Spruce and Pine) residues	Miscanthus sinensis		Bark + Wood sandwich structure	Oil palm trunk	Oil palm trunk strands	Japanese beech	Kenaf core	Kenaf core	Kenaf core	Sugarcane bagasse Pith	Sugarcane bagasse Rind	Bagasse pith	Bagasse	Oil palm trunk	Oil palm trunk	Core part of oil palm trunk	Oil palm trunk	Oil palm trunk	Palm date tree leaflets	Kenaf core	Kenaf core	Sugi Heartwood and sapwood	Bagasse	Whole coconut husk
Density ($g.cm^{-3}$)	1.44	1*	1.20	1.20	1.00	1.07	1.18	1.27	0.98	0.8*	0,8*	1.45	0.5*	0.35	0,15	0.75	0.75	1.35	0.75	0.8*	0.8*	0.8*	0.8*	0.62	0.97	1*	0.70	1*	0.75	1.35
TS (%)	-	23	-	-	12	18	15	9	9	22	32	12	11	11	10	200	10	7.5	7	47	42	20	18	25	150	20	35	20	14	8
WA (%)	1	43	5	11	40	45	26	23	-	51	59	8	23	-	300	-	-	11	-	105	80	60	70	-	100	41	20	45	-	8



Note: An asterisk (*) in the density line means that target density is reported and not the actual density measured.

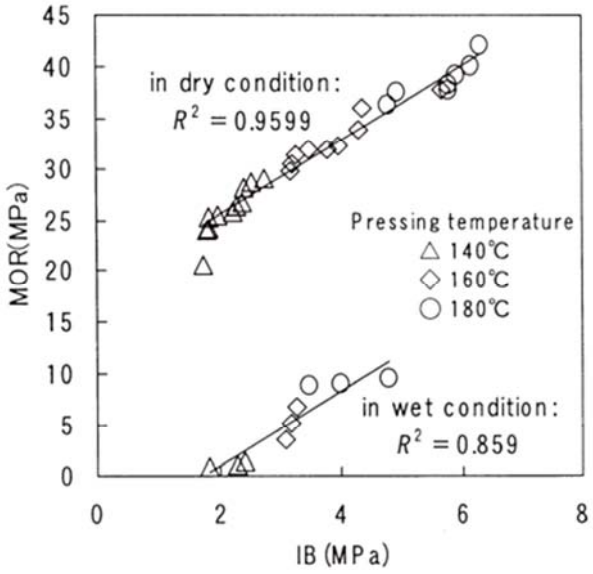


Figure I - 1: Comparison between dry and wet mechanical properties (Okuda and Sato 2004, republished with the kind permission of the Japan Wood Research Society)

I.2 The effects of plant materials origin on the molded specimens

I.2.A Reported Molded Materials

The effect of the nature of plant material is a very delicate parameter to study because materials and methods are rarely comparable between different studies reported in the literature, and most of the time researchers tend to focus on just one plant. Also, comparison focusing on one plant from one study to another cannot be considered 100% reliable, as plant varieties, harvesting season, growing sites, etc. will create heterogeneity (Saito et al. 2013).

Mason indicated that the Masonite disintegration process could work with pretty much whatever "ligno-cellulose material" (Mason 1926a). Then for molding Masonite®, it is reported that lignin is necessary for cohesion; therefore only materials containing sufficient amounts of lignin after steam explosion would be suitable (Mason 1928).

Although wood is the only material present in the examples given in their patent, Runkel and Jost (1956), considered that whatever "substances of vegetable origin which contain resinogene groups and active carbonyl compounds or which can form such groups" could be molded without using a pretreatment. On the other hand, Anglès et al. (2001) mentioned that boards from non-pretreated residual softwood could not be molded, and that thus steam pretreatment was needed. Other wood materials were successfully molded using steam pretreatment (Suchsland et al. 1987) or not (Ando and Sato 2010). The groups of Miki and Takahashi also investigated the possibility of molding wood at high pressure using steam (Miki et al. 2003; Takahashi et al. 2009) and bulk bamboo (Yamashita et al. 2007). Also cedar wood, bamboo rice straw, ginkgo biloba leaves, and coffee bean residues were densified into pellet fuels by high pressure molding (Matsuura et al. 2012)

The oil palm tree is a vastly studied biomass. Suzuki et al. (1998) and Laemsak et al. (2000) molded steam-exploded particles of oil palm tree fronds, and Nadhari et al. (2013) studied trunk particles treated in an autoclave. Different parts of oil palm tree (Hashim, Nadhari, et al. 2011) and date palm tree (Saadaoui et al. 2013) were also molded without steam.

The pith fraction of sugarcane bagasse was successfully molded without steam treatment, and satisfactorily results were obtained (Mobarak et al. 1982; Widyorini et al. 2005).

Kenaf core is another quite extensively studied material that was successfully molded without steam (Okuda and Sato 2004) and also using steam injection pressing, which made it possible to obtain low-density boards (Xu et al. 2004).

Miscanthus and banana bunches were also molded into boards with the help of steam pretreatement (Velasquez et al. 2003; Quintana et al. 2009).

As a conclusion, no general trend can be extracted from these results. The availability of waste plant material in one region often appears to guide the selection of materials to be studied and comparisons between plants remains rare.

I.2.B Different parts of plants

Type of plant tissue, cell wall structure and composition

Hashim et al. (2011a) compared the moldability of different plant tissues from the oil palm tree. In the same processing conditions, without pretreatment, the bark and leaves performed poorly, while fronds and trunk were much better. Bark cells had thick and rigid cell walls and were not deformable enough to be molded. On the opposite, parenchyma is a spongious tissue of plants, consisted of living cells with a high lumen to cell wall dimension; this structure was claimed to be responsible for good molding capacity of fronds and core part of the trunk of oil palm tree. Consistent results were also reported on date palm tree (Saadaoui et al. 2013).

Mobarak et al. (1982) also observed that bagasse pith (parenchyma cells) had better molding capacity than depithed bagasse (less parenchyma cells). Also the pith part reacted to pressure (higher pressure increased the bending strength), although depithed bagasse had the same poor properties with higher pressure. The same conclusions were reported on kenaf core (Okuda and Sato 2004) or coconut husk (van Dam et al. 2004).

On the other hand, it was shown that whatever the conditions, sugi heartwood had more than twice better mechanical properties compared with sugi sapwood on 1 mm powder binderless boards processed without steam (Ando and Sato 2010). Heartwood is the center, older, tougher part of the trunk, constituted of dead cells of higher lignin content. This result appears quite contradictory compared to the previous ones unless chemical differences (probably lignin and extractives) are considered. No difference was observed between heartwood and sapwood when ground to 10 µm and used as a binder for plywood for what was concluded that the grinding treatment cancelled the differences of cell wall structure.

Particle geometry and the need of steam treatment

A comparison of hot pressing and steam injection pressing on the parenchyma part (pith) and non-parenchyma part (rind) of bagasse showed no effect of steam for the pith fraction but a positive effect of steam for the rind fraction (Widyorini et al. 2005). This would explain the results of many researchers who necessarily employed steam for molding non-parenchyma tissue and also the good properties and many studies showing a high interest for kenaf core and other parenchyma parts of plants.

Remnants of storage polymers and agroindustrial by-products

Different agricultural or industrial plant residues are to be found in different countries, but a certain attention can been directed towards agroindustrial byproducts that would contain significant amounts of storage polymers, namely starch and proteins. Hashim et al. for instance worked on oil palm tree residues containing small amounts of starch. They first managed to obtain satisfactory mechanical properties using strands of 3 to 5 cm long, and the SEM photographs showed an homogeneous blend of the cells and melted and compressed starch granules (Hashim et al. 2010). In a second study on different parts of oil palm tree, the IB was quite well correlated to the starch content; starch was able to melt and provide a matrix effect, bonding the fibers together like in a composite material (Hashim et al. 2011). The starch granules were seen to fill the cell voids, sometimes unmelted in the compressed material even at an elevated temperature of 200°C; nevertheless, they were able to provide a bonding effect (Hashim et al. 2011; Lamaming et al. 2013). The melting of starch granules was confirmed after the materials had been steam-pretreated and molded at 220°C (Nadhari et al. 2013) or 180°C (Saari et al. 2014). The effect of starch as thermoplastic in situ binder has been reported to be significantly lower than sugars upon molding (Lamaming et al. 2013). Another example is to be found in the papers of Evon et al. (2010, 2012) who worked on sunflower cake, (which contains proteins) and reported on thermo-compressive molding of sunflower cake, and 3-D molding is easily accessible due to the thermoplastic behaviour of proteins. In this case, studied material is truly an agro-industrial byproduct, wherein the thermo-mechanical extraction of sunflower oil may play a role. Binderless boards were also successfully molded on jatropha seed oil cake (Hidayat et al. 2014).

Mixing / structural associations

Reports on mixing of materials are rare, and so are reports based on structural association of several plants. For instance, in order to counter-balance the poor flexural properties of bark fibers, Gao et al. (2011) introduced a mix of wood fibers (30%) and bark (70%) and tested different structural associations. They concluded that a homogeneous mixture added lot of strength compared to the control (100% bark), but the highest mechanical properties were achieved when they sandwiched bark between two layers of wood fibers. When using such a construction, the MOR and MOE were almost doubled compared with the control.

Contribution of lignin to water resistance

Many authors have made the hypothesis that lignin, on account of its hydrophobic nature, was responsible for most of the water resistance observed on specimens (e.g. van Dam et al. 2004a; Howard and Sandborn 1937; Okuda and Sato 2004). The addition of lignin was reported to drastically increase water resistance, which supports the previous hypothesis (Anglès et al. 2001). Additionally, it has sometimes been observed that lignin degradation was correlated with decrease of TS, showing that hydrophobic degradation products could work as native lignin; such observations could also support a hypothesis proposed by Ito et al. (1998b) to the effect that lignin was not responsible for the dimensional stability triggered by the high-severity steam pressing treatment. Also, the link with steam treatment could be made, as it was reported that steam treatment increased the relative lignin content by degradation of other components, and the correlation to the increase of lignin was made with an improvement of the mechanical properties (Quintana et al. 2009). More elements about this are reported later.

Contribution of hemicelluloses to water sensitivity

The fact that hemicelluloses must be eliminated for better water resistance was already mentioned in the pioneering works of Mason. The reduction of hemicelluloses content was performed thanks to a washing step prior to steam explosion, which effect was later confirmed by others (Howard and Sandborn 1937; Suchsland et al. 1987; Nadhari et al. 2013; Saadaoui et al. 2013).

Steam pretreatment and hot water extraction have been widely studied as a way to improve water properties of classical adhesive containing wood-based panels (Hsu et al. 1988). This effect relies on an improved deformability of wood particles and reduction of springback effect, both of which mainly can be attributed to the reduction of hemicellulose content (Pelaez-Samaniego, Yadama, Garcia-Perez, Lowell, and Amidon 2014). Comparable results were obtained in binderless pressing (Anglès et al. 2001). The hypothesis was also formulated that hemicelluloses' bonding effect could be responsible for water sensitivity of the molded products because of the hydrophilic nature of such bonds (Okuda and Sato 2004).

Finally, in the same way as the increase of lignin, the link between severity of pretreatment and a decrease of the relative content of hemicelluloses was made (Figure I - 2), and a correlation was established with an increase of the water resistance (Velasquez et al. 2003). The correlation between a decrease of TS and hemicelluloses content was verified by others (Widyorini et al. 2005; Quintana et al. 2009), which could possibly explain the improvement of water resistance observed by Ito et al. (1998a,b).

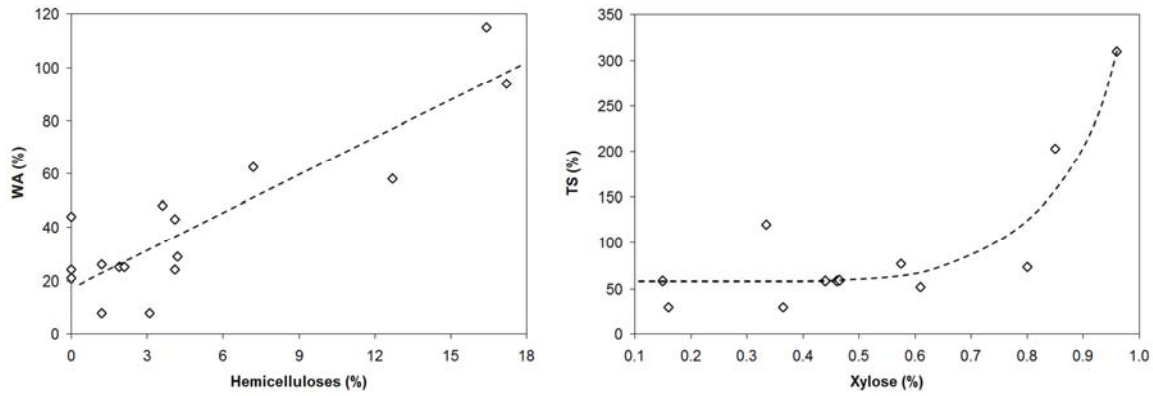


Figure I - 2: Correlation between loss of hemicelluloses and improvement of water resistance in binderless fiberboards, WA on the left (steam exploded miscanthus, adapted from Velasquez et al. 2003), TS on the right (steam exploded banana bunch, adapted from Quintana et al. 2009)

I.3 The use of steam in plant material processing

The first widespread usage of steam treatment for producing materials from natural fibers was in the manufacture of Masonite® (Mason 1928). Mason developed an apparatus called the Masonite gun (Mason 1926a; Mason 1926b) within which wood chips are steam pressurized during a certain time before rapidly releasing the pressure, and the material through a nozzle. A mechanical effect that breaks the structure of the fibers and leads to what is described as a defibrated and fluffy state is produced, cell walls are damaged, and inner plant cell wall chemical components made more accessible.

Steam-exploded wood fibers were processed into wet processed hardboard without binders, and Masonite® was industrially produced. Multiple applications were possible due to its high density, low cost, and relatively good water resistance. The product was also known as isorel, hernit, karlit, torex, or treetex. It was already claimed in the patent that

lignin and its accessibility were responsible for good mechanical cohesion and water resistance of the materials (Mason 1928).

The steam pressure, in the range of a few MPa (Table I - 5), is directly linked to its temperature. So basically, time and temperature (or pressure) are the 2 main parameters. A higher pressure and/or a longer time will produce more "changes" in the natural fibers, for which "severity" is a consensus term. Different materials can be produced by varying the severity (Mason et al. 1937). The time – temperature equivalence is described in the patent (Table I - 5), but it is also mentioned that a critical temperature should be reached.

The low energy requirements and eco-compatibility of steam explosion made it an interesting process for other applications than binderless boards, for instance for reinforcing the water resistance of the adhesive based panels (Hsu et al. 1988; Pelaez-Samaniego et al. 2013). Steam treatment was reported to increase the ethanol yield, lignin solubilization (Bundhoo et al. 2013), and also biogas yield production (up to 40%) despite some negative effects due to the generation of compounds inhibitory to micro-organisms (Zheng et al. 2014).

Table I - 5: First report of a time-temperature equivalence for steam pretreatement adapted from US patent 1,824,221 (Mason et al. 1937)

Time held at pressure	Temperature (°C)	Steam pressure (MPa)
30 minutes	216	2.1
5 minutes	231	2.8
105 seconds	244	3.4
60 seconds	254	4.1
30 seconds	271	5.5
15 seconds	285	6.9

Later, the time – temperature of treatment equivalence was formalized, and a combining variable called "severity factor" was created for more convenient comparison (Overend et al. 1987). This severity factor (also called R_0) has the following expression:

$$R_0[\text{min}] = \int_0^{t[\text{min}]} \exp\left(\frac{T[^\circ\text{C}] - 100}{14.75}\right) dt.$$

The consideration of the log R_0 imposes the prerequisite of the time - temperature equivalence, which remained an hypothesis that was questioned (Velasquez et al. 2003).

There are basically two ways of using steam in the processing of binderless 100% plant fibers materials:

As a pretreatment on the starting material separately from the pressing stage: In this case the very large majority of research works employed Mason's steam explosion approach (Mason 1926a; Suchsland et al. 1987; Velasquez et al. 2003). Some groups used a simple steam pretreatment in an autoclave without the mechanical effect of steam explosion, (Howard and Sandborn 1937; Takahashi et al. 2009; Nadhari et al. 2013). Others used steam in addition to more mechanical refining processes using disks or rolls (Xu et al. 2003; Gao et al. 2011).

As a processing aid, integrated in the pressing process, using a steam atmosphere surrounding a pressing machine (Ito et al. 1998; Widyorini et al. 2005; Miki et al. 2007) or injecting steam in the mold during pressing (Xu et al. 2003).

The benefits of steam treatment as a first step are often reported to be tremendous with respect to the mechanical properties. Anglès et al. (1999) for instance reported that steam-treated biomass succeeded, whereas non-treated biomass compressed materials were so weak they could not even be tested.

I.3.A The use of steam as a pretreatment: effects and optimal conditions on molded specimens

Mild severity optimum for strength

Optimal values of pretreatment (in order to maximize the MOR) are reported in Table 6, which shows that the average optimal value for log R_0 is about 4. Except for the last two examples in Table I - 6, the optimal value was quite uniform, despite the fact that different plant materials were being studied, including hardwood (Suchsland et al. 1987; Takahashi et al. 2010), fronds of oil palm tree (Suzuki et al. 1998; Laemsak and Okuma 2000; Nadhari et al. 2013), softwood (Anglès et al. 2001; Gao et al. 2011), and Miscanthus (Salvado et al. 2003; Velasquez et al. 2003), etc.

Velasquez et al. (2003) optimized temperature and time separately, and concluded that a lower temperature of pretreatment (200°C) and long time (6 minutes, log R_0 = 3.72) were the best conditions, and in doing so questioned the time - temperature equivalence (Overend et al. 1987). The pretreatment step was seen to have a higher impact than the other parameters during the compression-molding, statistically. Using the same methodology, similar conclusions were reported on steam pretreated banana bunches binderless boards, and it was also observed that higher severity led to a decrease of the bending properties (Quintana et al. 2009).

Table I - 6: Summary table of optimal steam pretreatment severity for producing self-bonded materials

Reference	Suchsland *et al.* 1987	Suzuki *et al.* 1998	Laemsak and Okuma 2000	Anglès *et al.* 1999	Velasquez *et al.* 2003	Salvado *et al.* 2003	Gao *et al.* 2011	Takahashi *et al.* 2010	Nadhari *et al.* 2013	Saari *et al.* 2014
Pretreatement type	Masonite gun + refiner	Batch steam explosion	Steam explosion	Continuous steam treatment	Batch steam explosion	Batch steam explosion	Mechanical refiner + steam	Autoclave	Autoclave	Autoclave
Steam temperature (°C)	229	224	224	217	216	203	188	180	120	130
Treatment time (min)	2.5	5	5	2.8	5	7.3	3.5	20	46	30
log R_0 (min)	4.2	4.35	4.35	3.89	4.11	3.9	3.14	3.66	2.25	2.36

High severity decreases MOR and MOE but is positive for IB and water resistance

Some papers have reported that severe conditions of pretreatment lead to lower bending properties (Suchsland et al. 1987; Suzuki et al. 1998; Laemsak and Okuma 2000). Suchsland et al. (1987) also reported that high severity of pretreatment appeared to increase the bonding ability, but the hypothesis was made that the shortening of the fibers could hinder this effect, which would explain a decrease on the bending properties. The mechanism was clarified later, with the measurement of a reduced cellulose content and lower degree of polymerization, which made it possible to conclude that the partial hydrolysis of cellulose caused by an excessive severity of treatment was responsible for the lower mechanical properties (Anglès et al. 2001). Later, the IB was actually confirmed to be maximized at high severity of pretreatment, and a higher proportion of fine particles produced during

pretreatment at high severity was suggested as an explanation to higher IB values (Velasquez et al. 2003). Low temperature of pretreatment was claimed to preserve the integrity of the fibers during pretreatment, although high temperature during the pressing stage for a short time was seen to be the best strategy for triggering the bonds without degrading the material too much. This was verified by optimization experiments, which were conducted to achieve a maximum IB for higher values of severity than for MOR / MOE, with the maximum value of 3.7 MPa (245°C) for 7.3 minutes (log R_0 = 5.13) (Salvado et al. 2003). Consistent results were obtained on banana bunches, wherein the IB was also demonstrated to be statistically dependent only on the pretreatment severity (in related experimental conditions) (Quintana et al. 2009). The maximum IB would be with a pretreatment severity factor of 3.55, which is lower than values reported by the other authors. The same kinds of results were reported using a steam-pressurized disk refiner, for which high pretreatment severity maximized the IB, while at the same time the MOR was decreased (Xu et al. 2006).

Positive effects of steam explosion on the water resistance is a classic of the adhesive bonded panels (Sekino et al. 2005). Mason reported good properties of Masonite (binderless hardboard) against water (Mason 1928), and had another patent on an more intensive use of steam explosion to produce water-resistant materials (Mason et al. 1937). The highest severity levels of pretreatment are uniformly reported to confer the highest water resistance (thus lowest TS and WA values). There is certainly a link to establish between self-bonding ability (IB values) and the water resistance (WA and TS values), as the optimal parameters for these variables are similar.

Unsurprisingly, steam autoclave treatment was also reported to provide good water resistance. A steam temperature of 180°C was reported to have a high impact, although further increase of temperature did slightly further increase the water resistance (Takahashi et al. 2010). In a lower range of temperature treatment, Nadhari et al. (2013) also reported the improvement of autoclave treatment on water resistance but concluded that optimal conditions of treatment should be 120°C and 46 minutes.

Steam pretreatment, flow behaviour and molding capability

Steam pretreatment has also been considered as a way of dramatically increase the flowability of plant materials, which is of great interest towards the production of objects of complicated forms in high pressure molding experiments.

A temperature higher than 160°C made it possible to measure the flowability of Japanese beech using a commercial capillary rheometer. The fluidity increased with temperature of pretreatment until 200 °C (Takahashi et al. 2009). Steaming temperature was demonstrated to first allow flow and secondly to lower the temperature at which the flow occurs. It was demonstrated that 200°C was an optimal temperature to impart fluidity, and the material could be made to flow at only 9.8 MPa of extrusion pressure. At 180°C of treatment, 29.4 MPa of pressure were needed to trigger flow. More generally, the lower the temperature of steaming, the higher has to be the pressure to trigger the ability to flow. A limit of temperature may exist, considering that the results at 220°C were worse than those at 200°C. The same conclusion was reached regarding the time of pretreatment, and the authors concluded that 10 minutes were sufficient at 200°C to trigger fluidity but increasing this time increased the temperature required for flow.

In a later study, Takahashi et al. (2010) correlated these results with the bending properties of their boards, which showed that molding in conditions over the flowing temperature / pressure of the material enhanced all of the mechanical properties that were considered.

I.3.B Steam as a processing aid: effects and optimal conditions

Steam atmosphere pressing

The steam atmosphere pressing technique involves use of a pressing machine wherein the mold is surrounded by a pressurized chamber where heated steam can be injected. A prototype built by HISAKA corporation was used in several studies (e.g. Ito et al. 1998a; Miki et al. 2007a). According to Miki et al. (2007a,b, 2008), the main difference and explanation of the better results of steam atmosphere pressing results from the steam saturation of air surrounding molded materials, which prevents moisture from escaping. The prevention of loss of moisture during the molding process would therefore be a major advantage to this technique. Steam atmosphere pressing also produced improved water resistance (Ito et al. 1998; Miki et al. 2008).

Widyorini et al (2005b) used a custom-designed porous metal pressing machine in an autoclave chamber, gluing together 2 veneers of kenaf core. At 1 MPa (=> 180°C) of steam pressure, 10 minutes was an optimum bonding time, whereas at 1.5 MPa (=> 198°C), 1 minute was optimum. However, best mechanical bonding was achieved with 0.8 to 1 MPa for 10 to 15 minutes.

Steam injection pressing

Steam atmosphere pressing entails a high cost of time and energy, as the whole chamber needs to be pressurized and depressurized at each cycle. Alternatively, as airtight molds are quite easy to build, another possibility is to inject steam directly into the material while it is being pressed in the mold. Originally, steam injection pressing was designed with the idea of maintaining a certain moisture inside the mat to improve thermal conductivity and heat transfer from the plates (Kelly 1977; Back 1987).

The group of Kawai et al. (main results in Table I - 7) first studied the possibility of molding binderless particleboards from kenaf core using a steam-injection pressing method (Xu et al. 2003). Steam is injected in the mat at a pressure from 0.6 to 1 MPa during the whole pressing stage. The IB and bending properties were reported to be much higher compared to hot pressing, and these properties increased with steam pressure. Treatment time had a low impact.

Table I - 7: Examples of conditions and mechanical properties of steam injection pressing experiments for production of self-bonded materials

Reference		Xu *et al.* 2003	Xu *et al.* 2004	Widyorini *et al.* 2005b	Xu *et al.* 2006
Plant material		Kenaf core	Kenaf core	Sugarcane bagasse rind	Kenaf core (pretreated)
Steam injection (MPa)		1	1	1	1
Time (min)		10 - 15	7 - 10	6	10
Target density ($g.cm^{-3}$)		0.7	0.1 - 0.3	0.8	0.5
Apparent density ($g.cm^{-3}$)		0.65	0.15 - 0.25	0.75	-
Properties (MPa)	IB	0.6	0.15	0.2	0.55
	MOR	16	2	5	18
	MOE	3	0.5	1	2.3

In the first paper (Xu et al. 2003), delamination was reported in the case of higher density boards, which was explained by a steam pressure imprisoned in the material that exceeded the IB of the material, making the boards explode when opening the press. Usually, binderless boards with density lower than 0.7 are not reported because of insufficient mechanical properties. Yet, Xu et al. (2003) reported a good correlation between density and the mechanical properties on binderless particleboards with density from 0.35 to 0.65 g/cm^3. Other results at lower density (0.15 to 0.3 g/cm^3) (Xu et al. 2004) followed the same mathematical law as previously reported data, as can be seen in Figure I - 3. The addition of a pretreatment step with a steam-pressurized disk produced fiberboards of very good properties with a low density of 0.5 g/cm^3 (Xu et al. 2006).

Steam pressing produced specimens (bagasse binderless particleboards) with values of TS mostly within the range 150 to 200% for conventional pressing and under 25% for materials made by steam pressing (Widyorini et al. 2005). Dramatic benefits of steam-injection pressing were reported elsewhere, e.g. for kenaf core binderless particleboards (7.47% to 11% of TS were obtained compared to 169% without steam) (Xu et al. 2003; Widyorini et al. 2005).

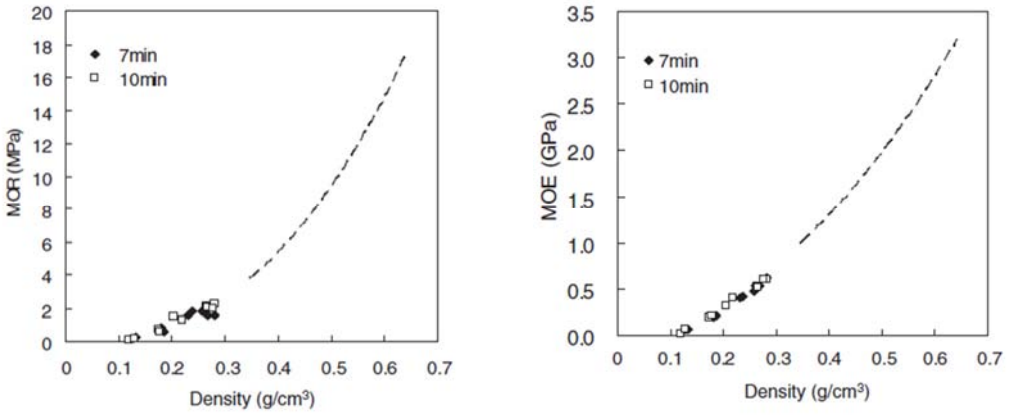


Figure I - 3: Example of correlation between MOR / MOE and density on a wide range of density from Xu et al. (2004), where the dotted line is modelling from Xu et al. (2003), all results on steam injected binderless particleboards from 5mm chips of kenaf core. Figures republished with the kind permission of the Japan Wood Research Society

Steam injection pressing, water resistance and boards' thickness

In the industry of wood-based panels with adhesive, it is well known that the volume / surface ratio has an effect on the WA and TS values. Under the same processing conditions, thicker binderless boards are reported to have better TS values, and thinner boards better WA (Suzuki et al. 1998; Laemsak and Okuma 2000). The explanation relies in the fact that the density gradient is generally less in thin boards, and higher porosity on thicker boards allows more water to infiltrate without making the board swell, which is why the comparison of water resistance is reliable only for boards of similar thickness (Okuda and Sato 2006).

A consistent observation was made on low-density steam-injection pressed binderless boards made from kenaf core, because of low density (0.25 g/cm^3), high WA values of 290% can be obtained on boards with very low TS of 9% (Xu et al. 2004), which would pass the JIS standards if the standard covered this sort of special boards (JIS A 5908, 2003).

I.4 Thermo-compressive process parameters and their effect on properties of molded specimens

I.4.A Molding pressure

Clarification of the relationship between pressure / density / target density

In the industry of wood-based panels, woods with bulk density lower than the resulting particleboards should be used because there is a direct correlation between the compression ratio and the boards strength (Kelly 1977). The purpose of pressing is to bring the particles close to each other while the resin is being cured, which provides thickness control. A "target density" is thus considered, when the mass of material introduced in the mold and the thickness of the product are controlled. This can be achieved, for example, in old presses by use of a metal frame (often called stop bars) that prevents the pressing machine from compressing further than the desired thickness. In classical particleboards densities range from 0.6 to 0.7 g/cm^3, while in classical fiberboards the values range from 0.65 to 0.85 g/cm^3, for instance.

When no glue is used, the generation of an in-situ binder or some other interparticle bonding phenomena is necessary for the product to keep its shape. In fact, because of the lack of binder, a springback effect is often observed in much higher proportions in binderless molding than in traditional resin-based wood-panels (Boon et al. 2013). When unloading the press, the material expands, depending on whether its IB is sufficiently high to retain the particles in their compressed form. Residual mechanical stress remains and produces boards with final density lower than the targeted one. This is why these have to be considered separately. The final densities observed in binderless boards (in general) are higher, ranging from 0.8 to 1.35 g/cm^3. In the industry of wood-based panels with adhesives (thickness control), the initial pressure is impacting the pressurization speed, that has an important effect on the vertical density profile (Kelly 1977) which is different than directly applied pressure. In this case, material can be compressed more than the desired density, but with the springback effect it was possible to obtain a satisfactory density; a good explanation of this effect can be found in the work of Gao et al. (2011).

Effect of pressure: Board manufacture with target density

Common sense suggests that higher density boards will express better mechanical properties (Suchsland et al. 1987). Even though this seems like an easy relationship, some tricky results can be found in the literature. The same author, for instance, once reported a good correlation (Anglès et al. 1999) and elsewhere did not observe any correlation (Anglès et al. 2001) when boards with about the same density exhibited variable mechanical performances. Also, in different studies of Hashim et al. (2010, 2011a,b) the authors suggested that increasing pressure could help to achieve better bonding properties. But while 5 MPa of pressure was used in two studies (Hashim et al. 2010; Hashim et al. 2011), 12 MPa of pressure were later used (Hashim et al. 2011), leading to better properties. Possibly, the 5 MPa of pressure was not sufficient to reach the target density, and the correlation should have been established based on density measurements. In parallel, when the resulting density is correlated to the mechanical properties, very good correlation has been observed (Okuda and Sato 2004; Okuda and Sato 2006; Ando and Sato 2009; Boon et al. 2013). In one paper (Figure I - 4) a non-linear correlation is reported; particleboards had low properties at low density, but after a certain threshold of density, properties increased and there was a linear correlation with density (Ando and Sato 2010). In this last case, an explanation was proposed concerning the improvements of the properties coming from the reduction of porosity when increasing density, which increased the thermal conductivity. One parameter

that has been barely studied is the pressurization speed, which is well known to modify the vertical density profile, classical in the wood-based panels with adhesive but almost never reported in articles concerning binderless molding. For instance, it was reported that thicker binderless boards had much lower IB than thin ones at comparable target density (0.8, 1, and 1.2 g/cm^3) (Suzuki et al. 1998; Laemsak and Okuma 2000) and the explanation to this probably resulted in the different density profiles, induced by thickness differences.

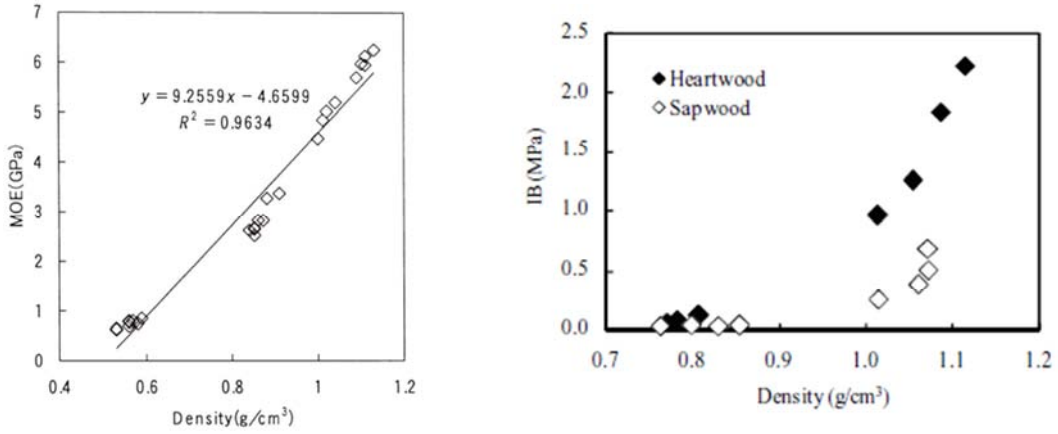


Figure I - 4: Example of correlation between mechanical properties and density of boards. Left graph (Okuda and Sato 2004) binderless particleboards from fine powder (53 µm) bagasse with a linear correlation, right graph (Ando and Sato 2010) particleboards from Japanese cedar milled through 1 mm screen with a non-linear correlation, republished with the kind permission of the Japan Wood Research Society

Effect of directly applied pressure (pressure control)

As opposed to "target density" experiments, pressure directly applied on the material without stopbars has been reported: Mobarak et al. (1982) were the first in the "modern area" to report on binderless boards. This paper first described a major effect of pressure on binderless boards manufacturing from bagasse pith and reported that mechanical strength of the boards was best at higher pressure (25.5 MPa) which is about 7 fold the usual pressure in the production of wood based panels (Figure I - 5). An effect of pressure was only observable for the pith part of bagasse, which is a non-fibrous tissue made of parenchyma cells. On every attempt, the density of the products was 1.35 g.cm^{-3} (about twice the usual density of traditional wood based particleboards), and it did not increase with increasing molding pressure showing that not only density (i.e. compaction) was responsible for the mechanical properties. But in addition, pressure must be triggering some destructuration and chemical reactions that bind the fibers together (e.g. switching the glass temperature transitions of polymers, increasing hydrolysis kinetic).

Ando and Sato (2009) used Kenaf core powder as an adhesive in plywood manufacture and showed that an increased pressure in the production of plywood gave better shear strength, as well as a quicker heating up of the veneer stack when wood cells were compressed. This was mainly caused by the significant increase of the board density when working without stop bars and, hence, producing boards with accordingly lower thickness at higher pressure. If the pressure exceeded a certain even higher limit, delamination occurred, because steam pressure created during the hot press cycle was not able to escape due to the tight material structure.

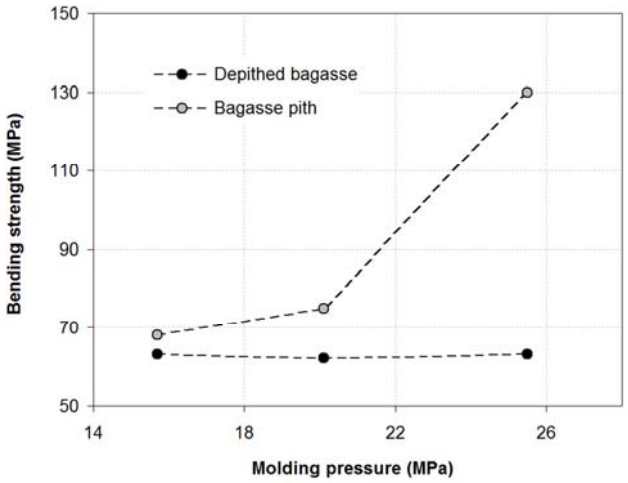


Figure I - 5: Correlation between pressure and bending strength (adapted from Mobarak et al. 1982)

High-pressure molding

Very high pressures cause a certain flow behaviour of pure plant materials. Extrusion tests on Japanese cedar powders were performed without any treatment (Miki et al. 2003). It was demonstrated that extrusion was possible at pressures starting from 70 MPa, whereby extrusion pressures close to 300 MPa were achieved in these experiments. Increasing temperature made it possible to reduce extrusion pressure. The relationship between pressure and bulk density of the extruded product follows a logarithmic curve with an inflexion point around 100 MPa (where obviously most of cell lumens have already collapsed) and a density limit tending to 1.4 g/cm^3 (Figure I - 6), which is close to the density of wood cell wall. The higher the pressure and the density, the higher are the mechanical properties.

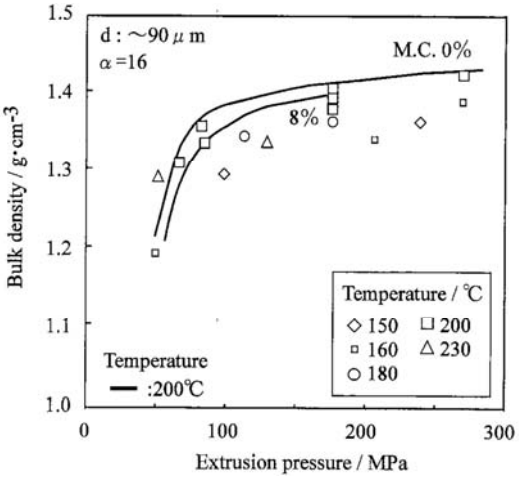


Figure I - 6: Correlation between extrusion pressure and density at high pressure extrusion of wood powders (reproduced from Miki et al. 2003, with kind permission of the Japan Society of Mechanical Engineers)

Later, wood powder was molded using high-pressure molding under a steam atmosphere, and pressure had a clearly positive effect on the shock-resistance properties (dynamic bending or Charpy impact) (Miki et al. 2007) whereas static bending tests, showed

a limited effect (Miki et al. 2008). Figure I - 7 summarizes these two results. The authors also noticed that using steam atmosphere pressing made it possible to reduce the pressure needed to mold wood powder into materials and got excellent bending strength up to 70 MPa with only 36.5 MPa of pressure. Using only 10 MPa of molding pressure resulted in 60 MPa of bending strength specimens.

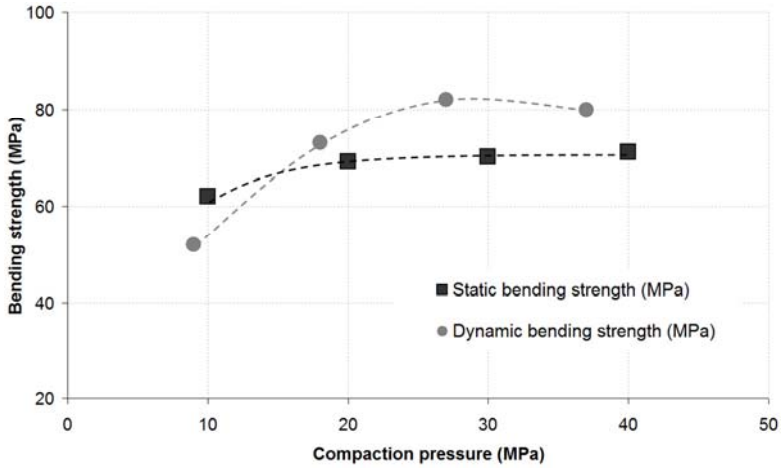


Figure I - 7: Correlation between pressure and bending strength in dynamic test (gray dots) and static (black squares) (adapted from Miki et al. 2007a and Miki et al. 2008)

Effect of pressure on pure cellulose molding

Recent papers have reported pure cellulose compression molding trials and the effect of pressing pressure. Within the range of 40 to 200 MPa, an optimal at 120 MPa was reported for maximizing bending strength (Rampinelli et al. 2010), whereas elsewhere no statistical difference was observed between 134 and 267 MPa of pressure (Pintiaux et al. 2013). Good results with a cold / hot two stages process were reported when using only 45 MPa of pressure (Nilsson et al. 2010). Pressing values from 0.7 to 2.5 GPa (Privas et al. 2013) were reported, but the researchers had to conclude that the pressure range was too high to observe any significant effect. Thus, a pressure bellow 0.7 GPa was sufficient to achieve the maximum density.

I.4.B Moisture content

Natural fibers are highly hygroscopic, and the water content modifies structural parameters such as crystallinity and lowers the glass transition temperature of its polymers (Célino et al. 2014). It is therefore an essential parameter.

Historically, according to the patent of Mason (1937), MC should be adjusted to 5% before pressing. A coproduct of the Masonite process was reported to have an optimal moisture content of 4% for molding (Howard and Sandborn 1937). Without using steam, an optimal moisture for producing compression-molded objects is reported as being between 5 and 25% and preferably between 8 and 17%, according to the patent of Runkel and Jost (1956), which suggests that moisture can be adjusted in quite a wide range. It was then reported that increasing MC had a negative impact on the mechanical properties (Table I - 8), but a minimum moisture was necessary to successfully mold products from bagasse (Mobarak et al. 1982).

Table I - 8: Moisture content and effect on the mechanical properties of molded bagasse products (density 1.34-1.36 g/cm^3) - (adapted from Mobarak et al. 1982)

Initial moisture	%	7.1	9.2	11.8	14.2
Moisture after pressing	%	6.6	6.2	6.4	5.9
Bending strength	MPa	67.8	66.1	63.8	60.6
Water absorption	%	13.3	15.1	18.2	21.7
Thickness swelling	%	10.5	12.9	15	17.2

Molding of dried (0% MC) plant material is generally unsuccessful, and many papers have reported that there is a need for a minimum MC, which is 3% according to Nadhari et al. (2013), but changing MC in the range ~10 to 30% seemed to have less effect on the resulting mechanical properties (Okuda et al. 2006a; Ando and Sato 2009). Nevertheless, high MC was reported to trigger delamination due to steam accumulation in the material during hot pressing (Ando and Sato 2009). The interaction between moisture and temperature is very important; for instance, in a high temperature range (200 to 280°C) the adjustment of MC to lower values (2 to 3%) produced good properties with a maximum at 260°C (Nonaka et al. 2013). In this study, the 200°C values were quite low, necessarily because of the low MC. These last results can be compared with the classical process in the industrial wood-based panels' production in which moisture is reduced in order to prevent reactions with the resin. In the industry, moisture is known to be impacting the density distribution which has never been studied in binderless boards experiments (Kelly 1977).

An increased MC was also reported to facilitate the flowability of wood powders (Miki et al. 2003) and bulk bamboo (Yamashita et al. 2007). Miki et al. (2003) also demonstrated that the increase of moisture shifted the temperature at which the bending strength was maximum: at 0 and 8% the optimum temperature was 195°C, although at 43% moisture 175°C was the optimal temperature. Finally, higher moisture produced significantly weaker materials.

The state of the plant cells has been reported to be different after extrusion (transfer molding), based on SEM observations; the cells were barely observable and had a "matrix" look, although with moisture the cells were still identifiable after molding (Yamashita et al. 2007). Moisture was concluded to ease the separation of the cells during flow testing at high pressure. The same observations was made later on different materials (Yamashita et al. 2009).

Okuda and Sato (2006) reported that the water resistance increased drastically with increasing MC of the initial material, because of a lower softening point of lignin (plasticization) and better heat transfer (Xu et al. 2006). The MC effect also was diminished at higher temperature of molding because softening point of lignin was already reached (Okuda and Sato 2006). However higher MC caused delamination on 0.7 g/cm^3 density boards (although 0.5 g/cm^3 density boards were correct).

Concerning pure cellulose molding, the authors' group has reported consistent results. Dry cellulose performed poorly, whereas 6, 8, and 10% MC cellulose had good and comparable mechanical properties (Pintiaux et al. 2013). Privas et al. (2013), on the contrary, reported higher modulus for dry samples, suggesting that, with very high pressure, moisture was prejudicial to the cohesion.

Temperature gradient, moisture, time and heat transfer

In the classical wood-based panels process, temperature is the energy source to cure the resin. Moisture has the role of facilitating the heat transfer from the plates to the inside of the mat and keeping the particles deformable (lower softening temperature of wood polymers in presence of moisture) for adequate resin/wood particles-fibers contact and target density (Kelly 1977). Temperature and moisture gradients exist inside the mat which has

been fully described in the industry standards but rarely reported in binderless boards experiments (Bouajila et al. 2005). In the surface layers, a certain evaporation takes place during the press cycle which permits to get close (~80%) to the plate temperatures (i.e. skin effect), whereas in the core layer, temperature remains close to the water evaporation temperature (depending on pressure, 105 to 115°C). Increasing pressing time increases the temperature inside the mat but the pressure increases, which can cause delamination. The same way, moisture reduction will reduce steam pressure but also heat transfer, this explains why these parameters have to be optimized together; this has been done in thousands of papers in the wood-based panels with adhesive, but characterization of such phenomena are still incomplete in the field of binderless boards processing.

I.4.C Temperature

Effect of pressing temperature on non-treated and steam treated materials

Temperature is often described as the most important factor in the production of binderless natural fibers moldings (van Dam et al. 2004). Thermal treatments are also crucial in the improvement of properties of wood composites, adhesive containing wood-based panels and self-bonded plant materials (Pelaez-Samaniego et al. 2013).

As can be seen in Table I - 9 which summarizes the conditions for which highest MOR was observed in different studies, research papers on non-steam treated binderless boards and high pressure molding are often reporting an optimal temperature between 180 and 200 °C, except for Shen (1986), who's material contained a high proportion of free sugars and Nonaka et al. (2013), who lowered the MC. Over this favorable range of temperatures, the mechanical properties are decreasing and/or delamination occurs (Ando and Sato 2009; Ando and Sato 2010; Hashim et al. 2011).

Some reports have concluded that increasing temperature had a high impact on increasing the IB of particleboards, which consequently led to the increase of the bending properties (Okuda and Sato 2004; Hashim et al. 2011).

A high temperature of pressing was reported to increase the water resistance and to be the most impactful molding parameter (Anglès et al. 1999; Velasquez et al. 2003; Ando and Sato 2009; Ando and Sato 2010; Hashim et al. 2011; Boon et al. 2013; Nadhari et al. 2013). Better results than equivalent UF or UMF bonded boards were once reported (Okuda and Sato 2006). The TS value went under 10%, which matches particleboards standards.

A higher range of temperature has been reported for steam-pretreated plant fibers (Table I - 10) than for non-treated materials. Low temperature molding processes are reported only for steam-pretreated fibers. In the absence of pre-treatment there is no or reduced possibility to produce objects at low temperature of, for example, 125°C (Suzuki et al. 1998; Laemsak and Okuma 2000). Still, a high temperature of pressing is also reported to have a positive impact on the mechanical properties of compressed specimens after plant fibers have been steam treated (Anglès et al. 1999; Velasquez et al. 2003). One report (Salvado et al. 2003) mentioned however that temperature had a limited impact on the mechanical properties from 195 to 245°C (which is still in a high range). Another report mentioned no effect of temperature on the IB but a drastic and positive effect on the MOR (Nadhari et al. 2013). Confronting these results, it seems difficult to present a general trend; also, for an unknown reason, most of the research works on steam pretreated material tended to use higher temperatures and reduced molding times (the time / temperature of molding equivalence is a classic for standard panels production).

Table I - 9: List of optimal temperature as reported in the literature for producing self-bonded plant materials without steam

Reference	Plant material	Process	Object	Target thickness (mm)	Final density (g/cm3)	Time (min)	Optimal temperature (°C)
Mobarak et al. 1982	Bagasse pith	Hot pressing 25.5 MPa	Particleboard	4	1.35	5	**175**
Shen 1986	Bagasse	Hot pressing 3.4 MPa*	Multipurpose	11.1	0.75	20	**240**
Nonaka et al. 2013	Bagasse	Hot pressing	Particleboards	9	0.8**	10	**260**
Hashim et al. 2010	Oil palm trunk	Hot pressing 5 MPa*	Particleboards	4.8	0.8**	20	**180**
Hashim et al. 2011a	Oil palm trunk	Hot pressing 12 MPa*	Particleboards	4.8	0.8**	20	**180**
Hashim et al. 2011b	Oil palm trunk powder	Hot pressing 5 MPa*	Particleboards	4.8	0.8**	20	**200**
Boon et al. 2013	Oil palm trunk	Hot pressing 5-10 MPa*	Particleboards	5	0.6**	20	**200**
Okuda and Sato 2004	Kenaf core	Hot pressing 5.3 MPa*	Particleboards	5	1**	10	**180**
Okuda and Sato 2006	Kenaf core	3 steps hot pressing 6+4+2 MPa*	Particleboards	5	0.8**	4+3+4	**200**
van Dam et al. 2004b	Whole coconut husk	Hot pressing	Multipurpose	N/A	1.4	3-30	**180**
Ando and Sato 2010	Japanese cedar	Hot pressing 5 MPa*	Plywood	4	0.8-1**	10-30	**200**
Miki et al. 2003	Japanese cedar	Extrusion at 178 MPa	Extrusion tests	N/A	1.4	N/A	**200**
Miki et al. 2008	Japanese cedar / cypress	Steam pressing 36.5 MPa	Multipurpose	N/A	1.4	45	**160**

Note: An asterisk (*) in the process line indicates the presence of stop bars, Two asterisks (**) in the density line means that the target density is reported and not the actual density measured.

Table I - 10: List of optimal temperature as reported in the literature for producing self-bonded plant materials with Process involving steam

Reference	Plant material	Pretreatment	Object	Molding	Target thickness (mm)	Final density (g/cm3)	Time (min)	Optimal temperature (°C)
Howard and Sandborn 1937	Masonite by-product	Masonite gun + grinding + washing	N/A	Hot pressing 13.8 MPa	N/A	1.44	10	176
Suchsland et al. 1987	Hardwood	Masonite gun + refiner	Particleboards	Hot pressing 2.76-5.52 MPa*	3.2	1**	1.3	215-226
Suzuki et al. 1998	Oil palm tree fronds	Steam explosion	Particleboards	Hot pressing 20-40 MPa*	6	1.2**	0.3	125-150
Nadhari et al. 2013	Oil palm trunk	Autoclave	Particleboards	Hot pressing 12 MPa*	5	0.8**	29	215
Anglès et al. 2001	Softwood residues	Continious steam treatment	Particleboards	3 stages hot pressing 4.2 MPa*	3.5	1.07	5-1-5	230
Velasquez et al. 2003	Miscanthus	Steam explosion	Particleboards	3 stages hot pressing 12 MPa*	3	1.18	5-1-18	180
Salvado et al. 2003	Miscanthus	Steam explosion	Particleboards	3 stages hot pressing 12 MPa*	3	1.1**	7.4	195-245
Gao et al. 2011	Bark + Wood	Steam thermomechanic. refinig	Particleboards	2 stages hot pressing 2.8-1.2	6.5	0.98	8	260
Takahashi et al. 2010	Japanese beech	Autoclave	Multipurpose	Hot pressing 30 MPa	N/A	1.45	10	180

Note: An asterisk (*) in the process line indicates the presence of stop bars, Two asterisks (**) in the density line means that the target density is reported and not the actual density measured.

As far as high pressure molding is concerned, temperature was demonstrated to increase the flow ability of wood powder but also increased the stiffness of the extruded products, with a maximum reached at around 180 to 200 °C (Miki et al. 2003). The thermal decomposition was thought to be responsible for better flowability during extrusion (Yamashita et al. 2007). In the case of high-pressure molding under steam atmosphere, 160°C was reported as the optimum temperature (Miki et al. 2007; Miki et al. 2007; Miki et al. 2008). As for cellulose molding, optimal temperatures have been reported at around 160 to 180 °C (Nilsson et al. 2010; Rampinelli et al. 2010).

Delamination process a conjugated effect of temperature and moisture content

The 180 to 200°C limit of pressing temperature, as reported previously, usually comes from delamination. It could be density dependent (Ando and Sato 2009) because low-density products would have sufficient porosity for the steam to escape. Delamination can occur in all sorts of plant material molding: particleboards, fiberboards, and high pressure molding (Rampinelli et al. 2010). In cellulose high pressure molding, the delamination limit was reported to be around 200°C (Pintiaux et al. 2013). Similar phenomenon was observed in high pressure extrusion of wood: lower density and lower mechanical properties are reported, and SEM observations showed cracks and bubbles (Miki et al. 2003).

To some extent, pressure can be released in the process by using a degassing phase, which is a classical procedure for standard panels production, described as a 3-step-process (i.e. compression degassing compression) e.g. used by Anglès et al. (1999) on steam exploded softwood for binderless fiberboards. The degassing phase made it possible for some authors to mold at temperatures exceeding a previously established temperature limit (Okuda et al. 2006a; Okuda and Sato 2006). With higher MC (20%) at 120°C of pressing temperature, the degassing could not prevent delamination. This showed that first, the degassing step is a limited solution, and secondly confirmed that the delamination phenomenon is caused by an interaction between moisture and temperature of pressing. The adequate control of MC and temperature and the understanding of their interaction is a key parameter (Nonaka et al. 2013). It was also demonstrated that sometimes cracks are not obvious (not observable on the outside of the material), and MOE and MOR values can be high whereas at the same time IB can be drastically reduced. Likewise, the water resistance and especially WA (increased) can be reduced under such situations, because water can more easily infiltrate into the samples. This observation is also a classic finding associated with standard panels production.

The cooling down of the specimen prior to releasing the pressure has been reported to work for preventing delamination (Yamashita et al. 2007; Miki et al. 2008). In some cases the cooling step was not sufficient to prevent cracks and bubbles, which were still observed on the materials. The cooling down of the mold between two pressing cycles is obviously a marginal option, as it is time and energy consuming.

Some papers have reported the application of vacuum to boards before unloading the pressure, which is easy in the case of a steam injection pressing apparatus, but the results were not satisfactory (Widyorini et al. 2005).

Pressing temperature and steam assisted molding

The examples of steam injection pressing all reported a molding temperature of 190°C, but such results have been limited to a few publications, all from the same research team. Actually, this value is the result of 1 MPa of injected steam pressure (183°C) plus a few degrees in order to prevent the water for condensing in the mold (Xu et al. 2003).

Pressing temperature, time and water resistance

The classic time / temperature equivalence suggests that the optimal pressing conditions could be either a moderate temperature of molding during a long time or a higher temperature for a short time. The effect of time was reported to decrease at high temperature (Anglès et al. 1999). Elevated temperature is also reported to allow the reduction of molding time at comparable board properties (Ando and Sato 2010). It was also observed that higher temperature resulted in boards having lower density, which was correlated to lower mechanical properties (Okuda and Sato 2006). But, this higher temperature improved the mechanical properties in the humid state, despite the fact that density was lower. More precisely, it was observed that increasing temperature led to increasing the WA but reducing the TS; this indicates that bond quality was better with a lower TS, but voids (cracks) were created in the inner structure, therefore increasing WA. Overall, and in a way comparable to the severity of steam treatment, it can be observed that optimal conditions for bonding (i.e. favorizing the IB) will also maximize the water resistance (Boon et al. 2013).

Skin effect

A special effect on the surface of materials obtained by compression molding is often reported (Runkel and Jost 1956; Mobarak et al. 1982; Suzuki et al. 1998; Laemsak and Okuma 2000; Anglès et al. 2001; Okuda and Sato 2004; Xu et al. 2004; Hashim et al. 2011; Nadhari et al. 2013). The inner part of this kind of material appears rough and mat-like, but the surfaces are, under certain conditions (elevated temperature but not exclusively), smooth, plastic-like, and shiny. The vertical density profile is a classical from the industry of wood-based panels with adhesive, but unfortunately it has been poorly investigated in the research works concerning binderless molding.

Effect of temperature in the particular case of free sugars containing materials

A free sugars binding system requires 180°C or more to achieve thermoset bonding (Shen 1986), and higher temperature leads to the best mechanical properties and water resistance of boards. According to Mobarak et al. (1982) and their trials on bagasse pith, highering temperature from 175 to 185 °C increased the bending strength by 9% but lowered water resistance, which could be explained some delamination as observed by many others. In this later paper, the best specimens had a WA of 11% and a TS of 7.5%, which are excellent values way over the average results. Sugar was also thought to be responsible for the good properties of bagasse molded at high temperature and lower MC (Nonaka et al. 2013). Consistently, the addition of sugars in oil palm trunk particleboards was reported to drastically improve the properties with twice lower TS and WA (Lamaming et al. 2013). Even more impressive, similar products were reported to be resistant to boiling in water (Shen 1986). This very particular behavior is certainly attributable to the in situ resin generated by reactions (decomposition and recondensation) of free sugars induced by high temperature. These include thousands of reaction oligomer products having up to 6 carbohydrates units and reactive furfural derivatives units (Golon and Kuhnert 2012).

Effect of temperature in the particular case of bark

The binderless molding of bark has been successfully reported between 205 and 300 °C (Chow 1975; Mobarak et al. 1982). The molding of bark at "classical" temperatures (180°C) consistently produced boards with very low properties (Hashim et al. 2011). A more recent study reported 240°C and 20 minutes as optimal conditions of pressing refined spruce

bark into boards, whereas 260°C was the best temperature for maximizing IB (Gao et al. 2011). These authors performed TGA analysis and showed that temperature was responsible for a higher weight loss in the material during pressing (up to 33%). In this paper, nothing more precise than "components were produced and responsible for selfbonding" was mentioned but if higher temperature is necessary for molding bark parts, the explanation may be the high content in polyphenolic compounds than can undergo radicalar polymerization.

Elsewhere, tannins have been investigated to serve as a binder for particleboards: Good results were reported with laccase assisted oxidation of tannins, wherein thermomechanical pulp was successfully bonded (Euring et al. 2011), and hydrolyzed tannins were reported to perform better than condensed tannins (Widsten et al. 2009). Ionic interaction and radical coupling were reported between tannins and wood fibers as bonding mechanisms (Widsten and Kandelbauer 2014).

I.4.D Time

Time of molding is quite often reported to be an interesting parameter for improving the mechanical properties, although it is quite tempting to try to reduce the time as much as possible to increase production speed. Some reports indicated that increased time is preferable for mechanical properties (Anglès et al. 1999) and water resistance (Okuda and Sato 2004; Nadhari et al. 2013), although a certain limit was reported to exist after 20 minutes in the bonding ability of kenaf core powder for a 4mm plywood (Ando and Sato 2010). Contradictorily, some researchers have reported that a short time of molding was preferable (Velasquez et al. 2003), which was associated with a high temperature of molding. Other reports showed that time has a limited impact on the mechanical properties (van Dam et al. 2004), which is consistent with high pressure molding of cellulose (Pintiaux et al. 2013). Another report mentioned 6 minutes to be an optimal time for a 1 mm thick cellulose plates (Rampinelli et al. 2010).

I.4.E Granulometry

Grinding is an energy-costly step, but lower particle size increases specific surface area and accessibility to inner cell wall components, which is positive for molding. Molding smaller particles also means that the strength of individual elements has less effect, and the bonding between the particles is responsible for most of the strength. Generally, reducing particle size is reported to have a positive effect on the mechanical properties (Shen 1986; Okuda and Sato 2004). The good effect of steam explosion could also partly rely on the generation of fines and global decrease of particle size because of the treatment (Suchsland et al. 1987). Molding bigger particles was confirmed to decrease the mechanical properties (Mobarak et al. 1982; Okuda and Sato 2006). Also, the introduction of bigger particles in fine powder was reported to degrade the mechanical properties, which were then comparable to 100% bigger particles (Mobarak et al. 1982).

Gao et al. (2011) obtained the best IB with finer particles (from 0.356 to 1 mm), but larger particles (> 1 mm) gave rise to higher MOE and slightly higher MOR boards. Consistent results were obtained elsewhere (Xu et al. 2006). The good adhesive strength of very fine powder (10 µm) was reported (Ando and Sato 2009) to be better than 1 mm particles, but the production of boards made of 10 µm powder failed (Ando and Sato 2010). This shows that a limit in the reduction of particle size may exist.

In some cases, bigger particles were reported to produce interesting properties (Hashim et al. 2010; Saari et al. 2014). In this particular case, strands of several mm long were compared to small particles (< 1 mm) under similar conditions of process and target density, but only bending properties were tested. Elsewhere, better water resistance was

obtained from chips compared to powder under the same operating conditions (Okuda and Sato 2006), but overall, few results can be found about the particle size effect. Conditions favoring higher IB usually have been shown to increase water resistance, but this seems not be the case for reduced particle size.

Concerning high pressure molding, Miki et al. (2003) demonstrated that higher particle size needed more pressure to be extruded. However, the bending strength of the products of 180 to 250 µm (small particles) and 90 µm (powder) was not significantly different. High shear subjected to the material might be responsible for leaving no effect of granulometry, as the particles were really deformed and rubbed one against the others. The same research group later reported an important result on the effect of granulometry in a steam atmosphere pressing process. The very fine particles did not perform strongly, and an optimum was observable around 100 µm particle size (Figure I - 8, Miki et al. 2007a). This somehow confirmed that a limit in reducing particle size would exist for optimal properties.

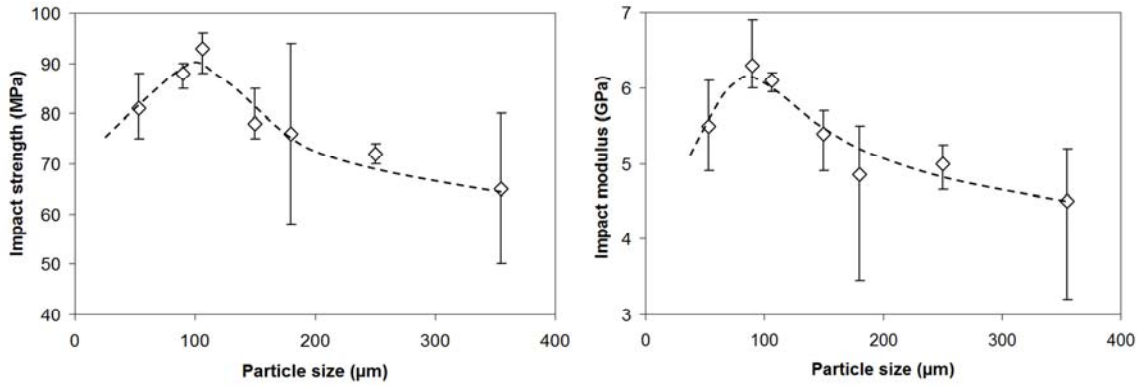


Figure I - 8: Effect of particle size on mechanical properties in high pressure molding under steam atmosphere (adapted from Miki et al. 2007a)

I.5 The physico-chemical changes and mechanisms of cohesion in self-bonded thermo-compressed plant materials

The molding phase is usually conducted at air equilibrium MC (between 5 and 12% and often 8 to 10% MC with room equilibrium) and temperature over 100°C; steam is thus created in the mold. Chemical changes occurring during hot pressing can thus be compared with steam pretreatements. The first thing to notice is that the molding time can be very fast if material has been pretreated (Suchsland et al. 1987; Suzuki et al. 1998), although short times of molding have not been reported on non-treated plant material. The pretreatment, however, takes some time to operate, and both processes, pretreatment + molding, or molding without pretreatment, can take about the same time. Runkel and Jost (1956) actually mentioned 2 phases in the molding of untreated natural fibers, considering a first step of production of gases from the material and their action on the material itself, and a second step of actual molding. The chemical modifications, however, were not reported in these early publications. Recent results have been bringing new data and highlights over the chemical changes occurring to explain the self-bonding ability of binderless plant materials which will be examined in this section.

I.5.A Physical changes

Change of color

During steam explosion of plant materials, a change of color, darker with higher severity of treatment, has been systematically reported, which suggests chemical changes (Mason 1926a; Hsu et al. 1988; Anglès et al. 1999). The same phenomenon is also observed as a result of an autoclave treatment (Takahashi et al. 2010) and on specimens produced by steam atmosphere pressing (T. Miki et al. 2007) and steam injection pressing (Widyorini et al. 2005). The same observations are made during classical compaction molding, darker with higher temperature and time of molding (Runkel and Jost 1956; Ando and Sato 2009; Boon et al. 2013). Obliviously, the change of color is a sign of degradation: the TGA analysis of plant fibers shows that hemicelluloses are the first to be completely degraded (240 to 300°C). Lignin starts to degrade at about the same temperature (240°C), but its degradation slowly proceeds until 700°C; cellulose on the other hand degrades in a narrow range of 320 to 380°C (Yang et al. 2007). The degradation occurring during hot pressing or steam treatment takes place at much lower temperature than the TGA results but conditions are too different (pressure, moisture, air) to conclude. Yet, degradation reactions and the change of colour are often associated with better mechanical performance and water resistance and common explanation for this is the generation of reactive compounds reacting on the fibers, with cross linking and condensation reactions.

Steam treatment and defibration

Pretreatment with steam is called "steam explosion" and "wood disintegration" (Mason 1926a; Mason 1926b), "steam treatment" (Anglès et al. 1999; Velasquez et al. 2002; Velasquez et al. 2003), or a certain type of "pulping process" (Suchsland et al. 1987), which name originates from the paper industry and the aspect of the fibers after treatment. Mason also used the term of "fibration" of wood (Mason 1926a) and described a "highly divided fibrous state" (Mason 1926b). The use of steam for defibrating has been since widely developed as refining method (also in a thermo-mechanical refiner) for the production of industrial wood-based panels (fiberboards and hardboards).

A low severity factor (e.g. 2.6) steam treatment does not bring any observable difference from the original fiber to the steam pretreated, but a higher (e.g. 3.8) severity factor produced fibers with similar length but smaller witdh, as can be seen in SEM photographs of Anglès et al. (1999). An individual fiber will be turn into a network of thinner single fibers with pretty much the same original length, thus increasing the aspect ratio length to width (Xu et al. 2006). The defibration is time and temperature dependent and mild conditions are considered the best option, as the fibers were described as becoming “long, light and fluffy” and not too much damaged.

Production of fines

After a Masonite gun treatment, 5 to 8% of fine solid material is discarded because this material would create defects on the surface of the Masonite boards; this fine material was molded and patented as a potential replacement for backelite (Howard and Sandborn 1937). Suchsland et al. (1987) reported about average fibers length and fines generation; steam treatment is not only increasing the aspect ratio, but also breaking down the fibers assembly, generating smaller particles. As seen earlier in this review, smaller particles (fines, i.e. ~ 0.2 mm and less) were seen to bring better performances (Shen 1986; Okuda et al. 2006b) and more precisely the IB (Xu et al. 2006; Gao et al. 2011), which is consistent with the steam effect on fines generation.

I.5.B Non-lignocellulosic parts chemical changes and effects

Weight loss, extractives and elimination of degradation products

The weight loss occurring during conventional hot pressing has not been clearly investigated, and it is in fact quite difficult to measure the weight loss due to degradation separately from a MC change. Hydrolytic reactions producing acetic and forming acids were reported (Mobarak et al. 1982), and autohydrolysis of plant materials has been described as a result of acids generated from their own degradation (Li et al. 2007).

The presence of high amounts of extractives (in the leaves) was thought to be prejudicial for mechanic performances, even if a high lignin content was measured (Hashim et al. 2011a). The authors made the hypothesis that extractives (e.g. chlorophyll) could hinder the bonding mechanisms. Other reports showed that removal of extractives prior to molding lowered the mechanical properties and the water resistance (Lamaming et al. 2013; Saito et al. 2013).

According to the Masonite corporation patents (Howard and Sandborn 1937), hemicelluloses are degraded with steam pretreatment, and products resulting from degradation are water-soluble. Therefore they can be rinsed out, which increases the strength and water-resistance of the products which is a classic of adhesive containing wood-based panels or composites (Pelaez-Samaniego et al. 2013). Hsu et al. (1988) reported that steam pre-treatment of wood chips increased the amount of water extractives, and a correlation of the "total solubilization" and log R_0 (scale for severity of steam pretreatment) was established (Table I - 11) (Anglès et al. 2001). Consistent results are found in other studies (Widyorini et al. 2005; Takahashi et al. 2010).

Table I - 11: Degradation and weight loss measured upon steam pretreatment severity (adapted from Anglès et al. 2001)

Exp. conditions											
Temperature (°C)	176	187	191	198	215	221	225	223	221	227	229
Time (min)	2.5	3.1	3.1	2.9	3	2.1	2.9	4.3	5.4	4.8	4.8
log R_0	**2.6**	**3.1**	**3.2**	**3.4**	**3.8**	**3.9**	**4.1**	**4.3**	**4.3**	**4.4**	**4.5**
Total solubilisation	**17.5**	**23.8**	**26.03**	**28.6**	**29.3**	**31.4**	**31.4**	**32.1**	**32.3**	**34.8**	**35.5**

A similar result was obtained with steam-injection pressing, and again the weight loss was correlated with steam pressure and time, which was an indication of degradation reactions during the treatment (Widyorini et al. 2005). A correlation was also established between IB and the weight loss (Xu et al. 2006).

I.5.C Cellulose and hemicelluloses changes

Cellulose and hemicelluloses degradation

Hydrolysis reactions leading to partial depolymerization of hemicelluloses and lignin are most likely to occur (Yang et al. 2007), and degradation products of hemicelluloses and lignin are confirmed in the water extractives from steam pretreated biomass (Sun et al. 2005). This was already mentioned in the work of Howard and Sandborn (1937), Suzuki et al. (1998), Tanahashi (1990). This hypothesis was also made for autoclave treatment of wood pieces (Ito et al. 1998).

Actual data confirmed the effective degradation of hemicelluloses and the positive correlation with severity upon steam explosion (Hsu et al. 1988; Quintana et al. 2009), steam injection pressing (Xu et al. 2006) with confirmation of xylose being measured in the water

extractives (Widyorini et al. 2005), and also concerning autoclave treatment (Takahashi et al. 2010). Degradation of hemicelluloses was also confirmed for classical hot pressing (Xu et al. 2006). For instance, Xu et al. (2006) measured 26.7% of hemicelluloses on refined fibers, 25.5% on the fiberboard resulting from hot pressing, and 20.2% when using steam injection pressing.

Cellulose is also thought to be degraded during steam treatments. The relative cellulose content was reported to decrease with increasing severity of steam explosion (Anglès et al. 1999). The alteration of cellulose was also demonstrated in another study (Anglès et al. 2001) where the DP_v (viscosity measurements of the degree of polymerization) was reported to decrease. Steam injection pressing was also reported to decrease alpha cellulose content, even though glucose residues were not significantly more extracted (Widyorini, Xu, Watanabe, et al. 2005). Consistently, the decrease of holocellulose content was reported using an autoclave treatment and confirmed as being positively temperature dependent (Takahashi et al. 2010). Cellulose degradation was not always observed, and some reports indicated a constant holocellulose content after steam explosion (Quintana et al. 2009).

Correlation of cellulose and hemicelluloses content and the physical properties

The basic idea is that hemicelluloses and lignin can undergo glass transition and will, hence, be responsible for the adhesion. Cellulose would not actively participate in the molding but rather serve as "reinforcement" for the lignin/hemicellulose matrix (Saito et al. 2013). But on the contrary, Ito et al. reported an important role of cellulose in the mechanisms of cohesion especially for water resistance. Steam treatment was observed to hydrolyze amorphous domains and turn cellulose crystal Iα into Iß (Ito et al. 1998a). In a second paper (Ito et al. 1998b) the authors concluded that steam treatment partially hydrolyzed even paracrystalline region of cellulose and that novel crystals were responsible for the shape fixation and water resistance. This findings were also confirmed by Tanahashi (1990).

Furfural and hydroxymethyl furfural routes hypothesis

When weak acid or water at 130 to 170°C is added to hydroxymethyl furfural, polymerization occurs (Mobarak et al. 1982; Shen 1986); this reaction could take place during hot pressing of natural fibers after some degradation of hemicelluloses, which is an old and motivating hypothesis (Suzuki et al. 1998, Runkel and Jost 1956). The furfural hypothesis has been often questioned and debated (Anglès et al. 1999; van Dam et al. 2004). However, few reliable chemical analyses have been published so far.

Okuda and Sato (2004) added 5 to 15% of furfural in their binderless boards, and they observed a small increase of IB. However, they could not prove a correlation between IB and amount of furfural addition. In a further study the authors suggested that furfural polymerization would not occur significantly (Okuda et al. 2006b).

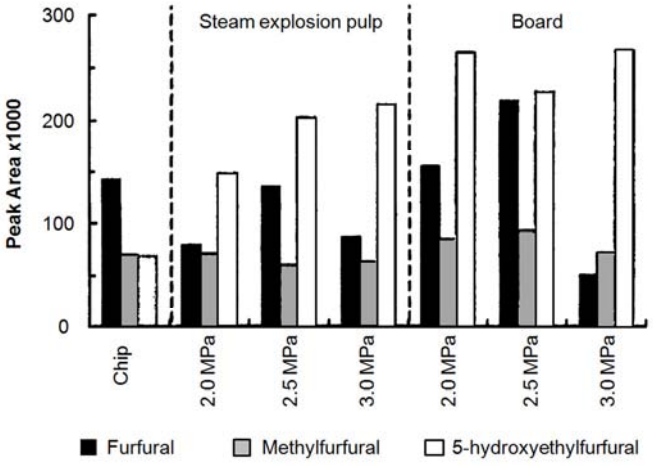


Figure I - 9: Furfural (and derivatives) content changes during steam pretreatment and molding (adapted from Suzuki et al. 1998)

Figure I - 9 shows that 5-hydroxymethyl furfural (HMF) content increased with pretreatment and was also higher in the board than in the steamed fibers (Suzuki et al. 1998). These results tended to verify the furfural hypothesis for the pretreatment step, but as furfural content increased after pressing, a possible polymerization remained uncertain. New results were reported recently which confirmed the formation of furfural and HMF during hot pressing from respectively pentoses and hexoses, and high temperature pressing made the HMF react to form new products (Cristescu and Karlsson 2013; Lamaming et al. 2013).

I.5.D Lignin changes

Lignin, according to Mason (1928), is the most important chemical for self-bonding and for water resistance of fiber-based binderless molded objects, Mason mentioned that during the molding operation, lignin melts and creates a welding effect.

Observation of lignin flow after steam pretreatment and matrix effect

The industrial thermomechanical refining process produce fibers bundles wherein the surface of the fibers is covered by lignin; the wet hardboard production process takes advantage of it by using lignin to form intra-fiber bonding (Back 1987). The explanation to this is in the moisture temperature conditions of thermomechanical refining over the softening point of lignin which preferably breaks wood structures within the lignin-rich middle lamella (up to 70% lignin content) producing holocellulose-rich units (fibers) encased in lignin (Irvine 1985). In binderless boards production, the use of steam-exploded materials other than wood was explored to produce fiberboards-like materials with the hypothesis of using lignin on surface of the fibers to create a matrix effect, the same way than in wet processing of hardboard, but at lower target density and in dry processing (Suzuki et al. 1998).

Lignin droplets were effectively observed on the surface of steam-treated fibers (Anglès et al. 1999). These lignin droplets came from the coalescence of lignin resulting from hydrolytic cleavage at high temperature which largely eliminates the lignin/cellulose interface (Marchessault et al. 1982). Their size was evaluated to be in the range 100 to 400 nm.

The conditions that made it possible to observe lignin on the surface of fibers also produced the best IB on the binderless fiberboards (Anglès et al. 1999; Gao et al. 2011). Consistently, a black matrix embedding the fibers, assumed to be the result of cross-linking of degradation products of hemicelluloses and lignin, was observed as a results of an autoclave treatment and during the pressing step; heat further allowed matrix components to flow out of the cell wall to fill the gaps between the particles (Takahashi et al. 2010). In the context of wood torrefaction study, recent results demonstrated that liquid lignin intermediate (LLI) migrated from the middle lamella upon thermal treatment and deposit on the fiber surface (Pelaez-Samaniego, Yadama, Garcia-Perez, Lowell, and McDonald 2014).

Lignin modification / degradation

Lignin polymer is reported to obtain an increased polydispersity upon steam treatment; the influence of refining temperature on the chemical changes on lignin is well known (Marchessault et al. 1982). Other literature reports (e.g. Figure I - 10 have indicated an increasing lignin content (Klason method) with severity of pretreatment (Lamaming et al. 2013; Quintana et al. 2009; Takahashi et al. 2010).

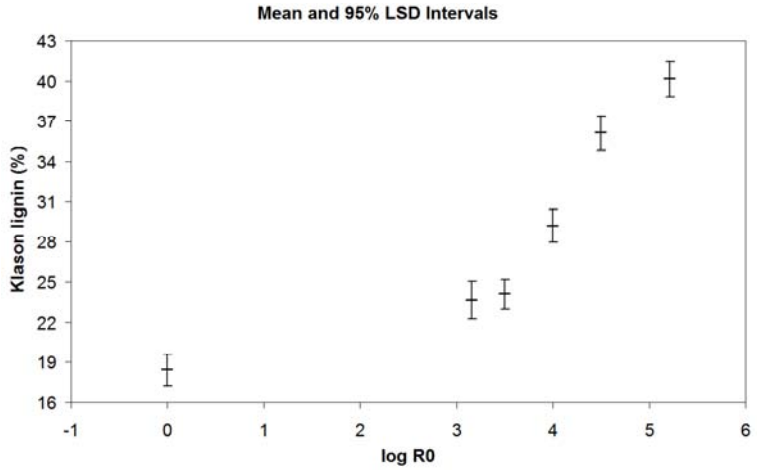


Figure I - 10: Link between the increase of lignin content and pretreatment severity (adapted from Quintana et al. 2009)

A particularly high Bjorkman yield (Björkman 1956) was reported after steam pretreatment, which suggested an increase of the relative apparent lignin content, including a lot of "esterified and etherified phenolic compounds" (Suzuki et al. 1998). According to the authors, those compounds are less likely to form covalent bonds; therefore they should not be responsible for adhesion. The cleavage of the aromatic nuclei of lignin was also reported at high severity, where the mechanical properties of molded products are decreasing. Lignin modifications due to steam pretreatment were confirmed by use of FTIR and NMR analyses (Suzuki et al. 1998; Laemsak and Okuma 2000).

Contradictorily, Klason lignin has been sometimes reported to decrease slightly with severity of steam pretreatment, while organic soluble components (soluble lignin) increased (Anglès et al. 1999). This fact was supported by steam injection experiments, as Klason lignin was reported to be degraded proportionally to steam pressure and time of steam pressing, while the relative composition in acid soluble lignin increased (Widyorini, Xu, Watanabe, et al. 2005). As far as hot pressing is concerned, degradation of lignin has been reported to increase with temperature, showing an increasing methanol yield (Okuda et al. 2006b). In this same paper, FTIR measurements showed cleavages of lignin intermonomer

linkages during hot pressing, demonstrating the degradation of some parts of lignin, which were thus more extractible with methanol and did not appear in the residue. This shows that these molecules did not create covalent bonds; they might nonetheless be plasticizers for lignin (Bouajila et al. 2005).

According to Widyorini et al. (2005c) the syringyl / guaiacyl (S/G) ratio decreased with severity of steam treatment, whereas in hot pressing conditions (without steam) the S/G ratio remained similar to the starting material. This showed that steam treatment degraded syringyl groups more than hot pressing. They also reported that the cinnamic acid / guaiacyl ratio (C/G) decreased with increasing severity of treatment and was well correlated to the strength of the composites. Tanahashi et al. (1990) proposed a complete degradation mechanism of lignin during steam explosion by treating extracted lignins, but the methodology remained unclear and no explicit conclusions were drawn.

Okuda et al. (2006a, 2006b), observed that the benzaldehyde yield of extraction decreased during hot pressing, showing that some lignin residues experienced condensation reactions. The authors claimed that guaiacyl acid could be the favorite molecule for condensation reactions. FTIR showed that new compounds were created, which confirmed reactions on lignin. However the crosslinking was not demonstrated in the cited work, and the authors mentioned that the condensation may occur to form small molecules instead of a real network necessary to obtain a matrix effect and thus explain the better bonding properties. Cristescu and Karlsson (2013) reported recently that beta ether and methoxyl groups subjected to condensation reactions corresponded to good adhesion properties and water resistance.

According to Ito et al. (1998a) the lignin content changes were not correlated to the water resistance of the square compressed wood logs materials. According to the authors, the mechanism of shape fixation against water relied more on cellulose crystallization than on lignin. Except for rare reports like the previous one, the hypothesis according to which lignin is important for selfbonding and strength of molded products is vastly supported (Mason 1928; Howard and Sandborn 1937; Suzuki et al. 1998; Bouajila et al. 2005; Imanishi et al. 2005; Okuda et al. 2006b; Yamashita et al. 2007). For instance, the addition of methanol extractives in fibers prior to molding increases the IB, while the material from which they have been extracted had a lower IB (Figure I - 11) (Okuda et al. 2006a). In this example, kenaf core powder with an average particle size of 53 µm was used and pressed into 0.8 g/cm^3 density binderless boards. The water properties also decreased with removal of those extractives, and improved upon addition. The addition of periodate lignin also enhanced the IB, while adding extracted holocellulose (therefore "diluting" lignin) led to its decrease (Okuda et al. 2006a).

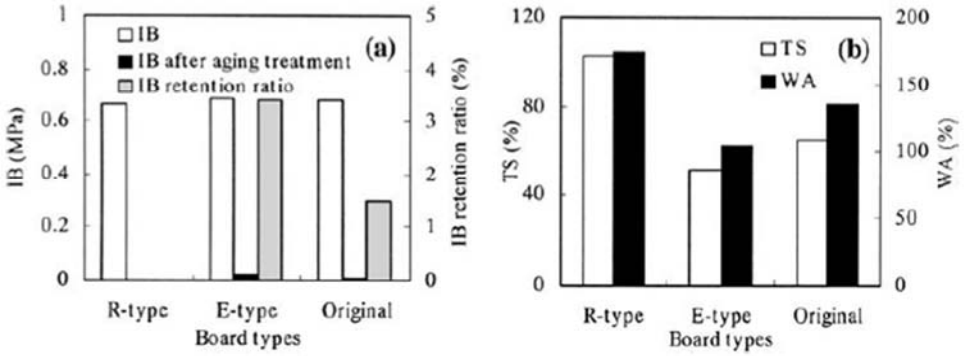


Figure I - 11: Experiment of methanol extractives (lignin components) addition (E-type) and removal (R-type) compared to original kenaf core powder (republished from Okuda et al. 2006a, with kind permission of the Japan Wood Research Society)

Lignin softening and "activation"

As mentioned by van Dam et al. (2004b) based on literature reports, steam explosion lignin and organosolv lignins are very reactive and can be used as adhesives for particleboards. They could replace up to 50% of synthetic binders (phenol / phenolic based resins, based on which an uncountable number of patents have been published), although the effective use for it remains uncertain on an industrial scale (Gosselink et al. 2011). The endotherm at 140°C that disappeared on a second heating was attributed by some authors to the softening of lignin, during which they believed irreversible condensation (dehydratation + crosslinking) happened (van Dam et al. 2004). Recent work on thermal analysis of lignin seems to attribute this first endothermic event around 150°C to the fusion of lignin. Some other high endothermic peaks above 180°C were associated with physical or/and chemical changes of lignin but are difficult to explain completely because of the structural complexity of lignin (Murugan et al. 2008; Kim et al. 2014). This irreversible change in lignin occurring after being heated over a certain temperature (180°C) would possibly be related to the "lignin activation" phenomenon previously reported (Mobarak et al. 1982). Activation is a term inherited from chemical (oxidant and/or alkali) wood treatments that would involve the partial depolymerization (modification of active sites) to obtain new linkage capability. Activated lignin would have a reduced melting point, and capacity to "polycondensate".

The effects of crossing the T_g value (softening point) by adjusting moisture and temperature have tremendous potential in increasing board properties. Bouajila et al. (2005) extensively studied the evolution of T_g of lignin in samples during hot pressing and reported that the mechanical properties mostly depend on the possibility for the molding temperature to exceed the T_g of lignin according to the local moisture in the material. Such experiments that are classical in the industry of wood-based panels with adhesive have been too rarely applied to binderless board production.

I.5.E Mechanisms of cohesion

In the industry of wood based panels, "adhesion" refers to the cohesive interaction between fibers and the adhesive, "bonding" refers to interactions within the adhesive, and "cohesion" is the sum of bonding and adhesion. In the case of hardboard, fibers/fibers cohesion only is responsible for the cohesion. In the case of binderless boards, the sum of fiber/fiber adhesion and insitu matrix adhesion and bonding is responsible for the cohesion and the science behind is still unclear compared to the classical wood-based panels technology. These differences appear to be important:

Plant materials have specific compositions, organization, and morphology that influence the molded objects properties in a much wider variety than wood.

Processing is generally made at higher temperatures for a longer time; thus many chemical reactions are possible: hydrolysis, degradation, oxidation, and recombination. These chemical changes that are undesirable in classical wood panels processing are in binderless necessary preconditions for self-bonding.

Compression of wood particles in the case of wood-based panels with adhesive is necessary, but pressure is an even more crucial parameter in the case of binderless boards processing: densities vary in a wide (mostly higher density) range although the density of wood based panels is calibrated (0.6 to 0.7 g/cm^3 for particleboards, 0.65 to 0.85 g/cm^3 for fiberboards).

In the classical wood panels industry, processing (i.e. pressing) is adjusting pressure time and temperature to evaporate excess of water and cure the resin. In the case of binderless molding, processing must be adjusted in order to trigger the bonding wherein all main parameters are interdependent: for example composition and structure of starting material will determine equilibrium moisture content, which will be determinant on the physico-chemical properties of fibers (glass transition temperature, flowability, crystallinity)

but also on the mechanisms of degradation of lignocellulosics components, and all this will be impacted by processing parameters especially time and temperature.

The comprehensive understanding of the exact mechanisms that would fully explain the properties of binderless plant materials is difficult, but there are some concepts and ideas that can help to improve their properties. There are some parallels to make between selfbonded plant materials and wood welding on the one hand, and thermal wood treatment in the other hand:

Glass transition of cell-wall polymers

The importance of glass transition in wood-based materials inherited from the polymer science and was extended to biopolymers in the early work of Slade and Levine (Slade and Levine 1991). All polymers undergo a transition from a glassy state to a rubbery state at a specific temperature, which is extremely dependent on their moisture content (Figure I - 12).

In the rubbery state, polymers acquire enough molecular motion to deform. They adapt to the mechanical constraints, which increases surface contact and creates a matrix effect inside the composite. Depending on their molecular structure and hygroscopicity (depending on the polar character of the polymer), the glass transition temperature (T_g) varies from around 200°C in the dry state to around 0°C for 20% MC for most carbohydrates. The T_g's of wood polymers in the dry state are reported to be 220°C (cellulose), 170°C (hemicellulose), and 200°C (lignin) (Back 1987). An illustration of the the T_g-moisture dependence is the possible molding of hardboard in wet process without using binders although binders are necessary in the dry state because core layer cannot reach the T_g of wood polymers.

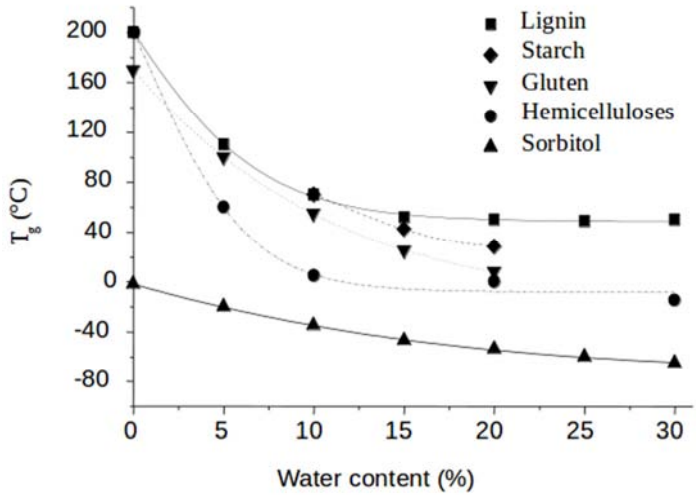


Figure I - 12: Glass transition temperature of biopolymers according to their water content (adapted from Gaudin et al. 1999; Micard et al. 2000; Slade and Levine 1991)

Yet, although isolated lignin and hemicelluloses are amorphous and exhibit glass transitions, their behavior inside the organized cell-wall structure is not as obvious (Irvine 1985), and it becomes even more complicated when they are partially or completely degraded into low molecular weight compounds, for which no thermoplastic effect could be reasonably taken into account. In many cases, the effect related to the glass transition depends on raw material structure, mechanical, chemical, and enzymatic pre-treatments (Álvarez et al. 2011), as all these effects influence molar mass and molar mass distribution of the material as well as secondary forces additionally responsible for the integrity of the material. Nevertheless,

the presence of lignin, free enough to show a relaxation peak when tested in DMA, is determinant to improve mechanical properties (Bouajila et al. 2005). The compression process on lignocellulosic fibers at a temperature above lignin glass transition temperature (which can go above 150°C when water is evaporated) gave the best properties. A parallel can be made with thermomechanical refining of wood that requires to place the fibers in moisture / temperature conditions above the T_g's of polymers (hemicelluloses, amorphous part of cellulose, lignin) in order to separate the fibers along the tangential orientation of other fiber direction and obtain higher surface development (Irvine 1985).

The thermoplastic behavior of biopolymers from plant cells have also been described for fibrous raffinate of sunflower containing residual proteins (Evon et al. 2010) and on wheat straw for the production of pellet by dry extrusion (Stelte et al. 2011).

Similar conclusions have been reported concerning the cohesion obtained by wood friction welding. Temperatures around 200°C are reached in the glue line, which is densified, and the thermoplastic effects of lignin and hemicelluloses are predominant (Gfeller et al. 2003).

Cross-linking of lignin-carbohydrate-complex (LCC)

In the field of wood treatment in order to increase its durability many research works have attempted to explain the mechanisms of chemical changes during a thermal treatment depending on the operating conditions. Factors considered have included the presence or not of oxygen or of water vapor, temperature, and time. These processes involve then clearly the same kinds of modifications as hot-pressing or wood welding.

Some of these findings are similar to those discussed in the previous part on the heat-induced degradation of lignocellulosic components: a reduction of free hydroxyl groups through the degradation of hemicelluloses (Srinivas and Pandey 2012; Singh et al. 2013; Liu et al. 2014), a decrease of cellulose content, like determined on bamboo samples (Y. M. Zhang et al. 2013), a change on lignin structure with an increase of the aromaticity (Park et al. 2013), but also some physical effects such as a decrease of nano-pore shares and fiber saturation point (Zauer et al. 2014).

The increase of durability of heat-treated wood (two stages, first in excess of water vapor then in a dry state under an inert atmosphere, temperature below 200°C) is mainly induced by cross-linking mechanism (Tjeerdsma et al. 1998; Boonstra and Tjeerdsma 2006). First the hemicelluloses are degraded, producing acids that further increase the depolymerization rate of carbohydrates (of the remaining hemicelluloses and the amorphous cellulose); then lignin is cleaved and activated with an increase of free reactive sites. In a second step, the cross-linking of the lignin network occurs, involving some products of hemicelluloses degradation such as furfural or methyl-furfural, which was confirmed in binderless particleboard production (Cristescu and Karlsson 2013; Lamaming et al. 2013). Polycondensation reactions are not completely elucidated but are thought to be responsible for the lignin content increase after heat treatment and obviously related to the improvement of water resistance.

Hydrogen bonding and cocrystallisation of cellulose as a consolidation mechanism

The most admitted hypothesis in binderless board production is that cellulose does not play an important role in bonding (Anglès et al. 2001). But, looking at the results obtained by hot pressing of pure cellulose, there might be a possibility of pressure-driven selfbonding in cellulose, as some mechanical properties obtained by direct compression at high pressure of cellulose powder have been reported (e.g. Pintiaux et al. 2013). The mechanisms of cohesion are thought to rely on fibril aggregation through hydrogen bonding (Nilsson et al. 2010) or other interactions, which has been recently debated (Glasser et al.

2012). Crystallinity changes were also observed (Vaca-Medina et al. 2013), which could confirm the importance of cocrystallization mechanisms (Newman 2004).

Conclusion and future directions

Production of binderless material by thermo-compression of lignocellulosic fibers is a very simple technique in front of a very complicated science: it requires studying many concomitant phenomena involving the disorganization and re-organization of complicated multi-components of biological structures. Most of the time, research studies on binderless boards do not take advantage of the classical phenomena that have been vastly investigated in the thermocompression of industrial wood-based panels with adhesive. In many studies, it is clear that the bridge between these two different worlds of science has not been crossed. Lots of improvements for this new kind of materials are still possible, and although the complete understanding of the occurring transformations remains unachieved to date, some elements that have been highlighted in this review will help to guide researchers who would like to study these fascinating transformations and improve future materials.

From the analysis of the literature, it appeared that correct mechanical properties can be obtained without pretreatment (i.e. particleboards type) in the case of certain raw materials, but when steam treatment is involved it seems that any lignocellulosic material would be moldable (i.e. in fiberboards type) and would result in suitable mechanical properties. Water resistance, however, remains low and does not match the standards on industrial wood-based panels. Regarding the choice of raw materials, the use of by-products is preferred and the presence of lignin (and eventually of storage biopolymers even in small quantities) is definitively favorable. Mixing plants together and structural associations (layers etc.) have been barely studied and could be of great interest.

The eco-friendly argument is very often offered as a competitive feature of such materials, but looking more precisely at the energy cost of such processing is necessary to qualify its eco-compatibility. There is a lot of room for Life Cycle Analysis of this kind of materials and processes, which should produce interesting and innovative studies.

Temperature of molding is undoubtedly the most important processing parameter for which the limiting factor is delamination. High temperatures are favorable to improve water-resistant properties and are responsible for the skin-effect and "plastic" touch. A minimum of moisture is necessary in order to obtain satisfactory mechanical properties, but this minimum value and the effect of higher moisture are still unclear. During compression at elevated temperature, steam is generated from the initial moisture, and effects can be compared to changes occurring during steam pretreatments. Some technological tricks can be applied to prevent delamination, but more research is needed in order to better understand the relation between moisture / temperature and delamination, because molding conditions that give the best properties are very close to those triggering delamination.

Steam treatment involves a combination of defibration, degradation (of hemicelluloses and part of lignin mainly), and lignin modifications (plasticization i.e. decrease of T_g, partial depolymerization, flowability, and condensation to a lower extent). Moderate severity of steam treatments generally provides the best bending properties. The highest severity of steam treatment was reported to increase water resistance and IB: these two parameters seem to be correlated, which could be further studied. In our opinion, a moderate severity of pretreatment in one hand and a higher severity in the other hand would favor two different mechanisms, that we named "thermoplastic" and "thermoset", respectively. These two main bonding mechanisms would happen in thermal treatment and any kind of thermocompressive molding of natural fibers, even at moderate pressure, which is not the case of the quite unknown cocrystallization phenomenon reported on high pressure molding of pure cellulose; and for this reason, is considered apart.

Thus, it makes sense to think in terms of a "thermoplastic" mechanism, which would mostly occur under mild conditions of processing (temperatures below 160 to 180°C), during which the glass transition temperature of lignin and hemicelluloses (and also starch and

proteins if concerned) is passed. In the resulting rubbery state, polymers would deform, filling the voids in and between particles, and giving the highest mechanical properties (MOR, MOE). The "thermoplastic" mechanism can be expected to occur more easily if polymers are freed up by chemo-mechanical destructuration and plasticization brought about by pretreatments because of the highly organized native state in the plant's cell-wall.

Secondly, one can envision a "thermoset" mechanism, which involves chemical reactions at higher temperature (over 200°C), with more important depolymerization / degradation of the polymers, leading to the production of weak acids and contributing to even more degradation by autohydrolysis. Highly reactive degradation products, especially aldehydes (particularly furfural and hydroxymethyl furfural), would participate (together with lignin) in the creation of new compounds (e.g. lignin-cellulose complexes) and in the cross-linking of the composite matrix, which brings about bonding between the cellulosic particles and gives rise to water-resistant properties.

Because of the gradients (density / moisture / temperature) occurring within the processed material, depending on product shape (e.g. thickness), temperature, moisture and time have to be adjusted together to control the thermoplastic/thermoset balance. Lignin for instance, which is reported to be the most important polymer for the development of bonding in the absence of an added adhesive, would have different behaviors: in the "thermoplastic" mechanisms lignin would be "activated", plasticized, and experience flow and some degradation, whereas in the "thermoset" mechanisms, condensation reactions would result in complexes with the other polymers. The "thermoplastic" / "thermoset" limit, however, remains unclear also because it is extremely complicated to study lignin itself, as extracted lignin is always degraded and would not behave as native lignin (as it is inside the cell wall).

Surely, the "thermoplastic" and "thermoset" mechanisms coexist, and no limit can be precisely set. Yet, delamination is thought to occur at the transition from "thermoplastic" to "thermoset". This is because of the loss of native structure due to thermoplastic flow and disorganization of the cell wall structure and the release of volatile compounds and water. At the same time more polymer/polymer interactions take place during the compression in the rubbery state, and these involve organic compounds produced in the course of thermal degradation. When the "thermoset" mechanism is predominant, water would be consumed by hydrolysis and volatile compounds would be condensed into bigger non-volatile structures. Much further work is needed towards the understanding of these physico-chemical reactions for these simple but elegant materials to find a real industrial market.

II Preliminary discussion about technical considerations

This chapter is an appendix of the experimental part (Chapter VI) yet a necessary preliminary to understand the techniques employed in this thesis to acquire the results and their evolution.

As seen in Chapter I, most of the literature about the thermo-compression of plant fibers concern industrial wood-based panels with adhesives or their alternatives that are focusing on replacing either the starting material (wood) or the binder system (different binder, or binderless molding). In the field of industrial wood-based panels and related materials, thermo-compression can be very restrictive because panels of fixed density and thickness are produced. Yet, this technic is not commonplace, and leaves a lot of room for innovations and imagination. Thus, the description of the molding process, definition of terms and some highlights on the technological locks are necessary for the reader to understand the problematic and all the complexity of this subject, and subsequent choices made in this work.

II.1 Project HYPMOBB: where it all begun

The LCA has been working with constituent's separation and treatments and modifications of biomass such as wheat straw for decades. The laboratory has gained a high expertise on the use of twin-screw extruders. When mechanically pretreating vegetable matters in a twin-screw extruder and investigating conditions, low solid/liquid ratio have been tested which conducted to the blockage of the extruder, usually in front of the dies which didn't let the material out. In this situation, pressure is increased, and friction occurs between the rotating screws and the extrusion chamber, which leads to rapid heat generation while the material keeps arriving, increasing shear and torque on the machine, that eventually stops. When disassembling the extruder, highly densified vegetable matters was found with a shiny plastic-like surface effect, perfectly fitting the shape of the screws (Figure II - 1).

Figure II - 1: Remains of wheat straw extrusion blockage

The hypothesis was made that 100% plant fibers self-bonded objects with a plastic finish high molding capacity could result from heat and pressure treatment. Thereafter was born the idea of project HYPMOBB to reproduce this extruder failure phenomenon, study and possibly exploit it.

II.2 Compaction molding, principle, design and terms

Compaction molding is defined as the technique which uses two complementary "male" and "female" shapes to form a molded object upon applying pressure between the two complementary shapes. It is commonly used in reinforced systems with thermosetting resins and glass fibers or more recently plant fibers.

II.2.A Two dimensions molding

In 2D molding, the two complementary shapes are flat and the starting material is loaded in the lower part called "frame". The upper part is called "punch" and enters the frame to apply pressure and form the compacted material (Figure II - 2).

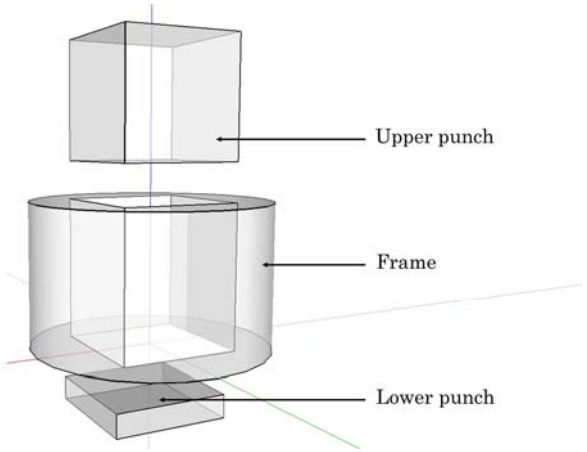


Figure II - 2: Drawing of a 2D mold (5x5 square shape)

II.2.B Three dimensions molding

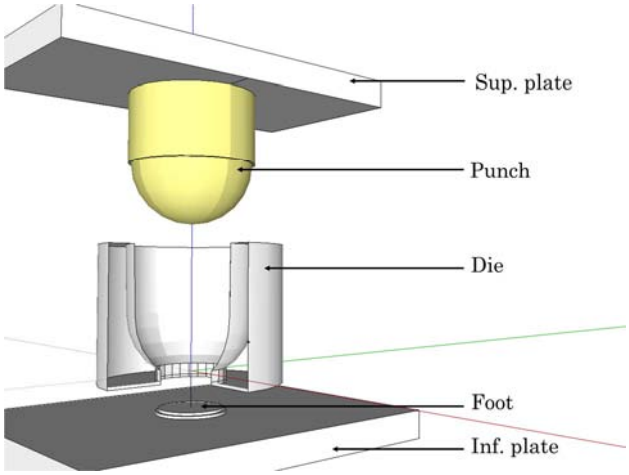


Figure II - 3: Drawing of a 3D mold (bowl shape)

In 3D molding, the female part is called "die" because it includes a prolonged part where the material is loaded before compaction. This prolonged part is necessarily an extruded length of the maximum diameter of the male part which is called “punch”. The part over this maximum diameter will thus be “printed” by the upper punch, whereas the die will be responsible for the shape of what is under the maximum diameter. For example, parts like bowls can be molded (Figure II - 3). For the need of demolding, the die should have an open part in order to help release the molded object from the mold. In the case of a bowl, the open part is on the foot of the bowl, and for stability reason, a relief is machined on the inferior plate in order to mold a hollow disk in the molded object.

II.3 Limits of compaction molding applied to lignocellulosic fibers

Direct compaction molding is a technique that has the advantage of being easy to set up, using simple and relatively light molds, simple pressing machines, allowing versatile experiments but also has some limits. Highlighting and understanding these limits is essential for considering technical applications and improvements.

II.3.A Limited shapes, not actual 3D

Because of this "die and punch" conception, only “semi-3D” shapes can be achieved. For instance, an "hourglass" shape cannot be molded in compaction-molding because, in the direction of the hourglass standing, the cross section (diameter for a round shape) goes through a minimum between 2 maximum thus it cannot be removed from the mold (Figure II - 4). On the contrary, a "bowl" shape is possible (the diameter has only one maximum).

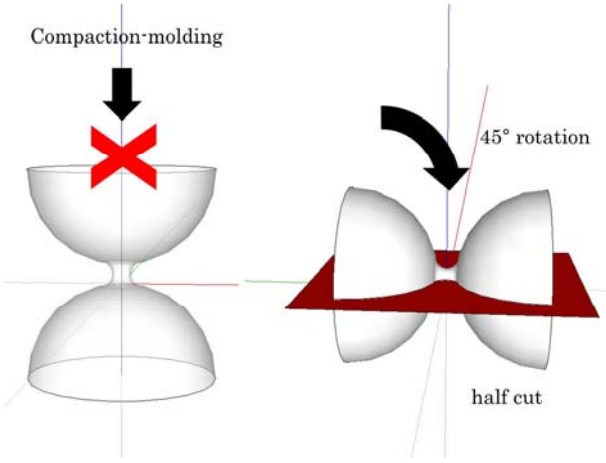


Figure II - 4: Semi 3D compaction molding, the hourglass example

The hourglass can be molded in the direction of the hourglass lying (alongside) which would require to precisely adjust the height (therefore the quantity and density of the material) very carefully.

Considering a perfect control is achieved on quantity and density of the material after compression, the machining of the punch would still be really uncertain as very tight edges are needed (in theory, infinitely tight) with the requirement of resisting to the high pressure (Figure II - 5). Even if these requirements are completed, the demolding would still be difficult; these considerations put on the light on the shape limitations of compaction molding.

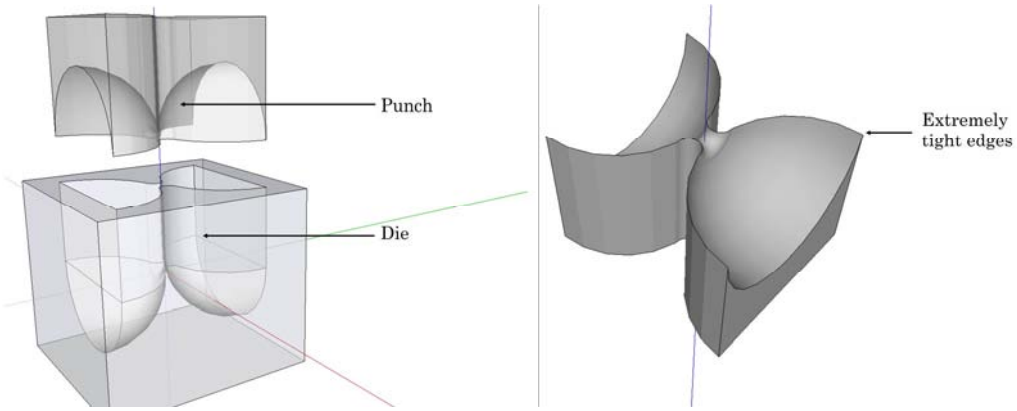


Figure II - 5: Drawing of an hourglass shape mold alongside and punch

II.3.B Demolding

Because of the conception of the molds, the molded part remains in the die (female part) and demolding has to be carefully designed. Manual ejection is possible if the mold can be put apart easily but it would take much time, what, for industrial application is limiting. Casual mechanical ejection technology (e.g. compressed air driven ejectors) cannot be used because the parts needs to be lifted up at least the height of the female part.

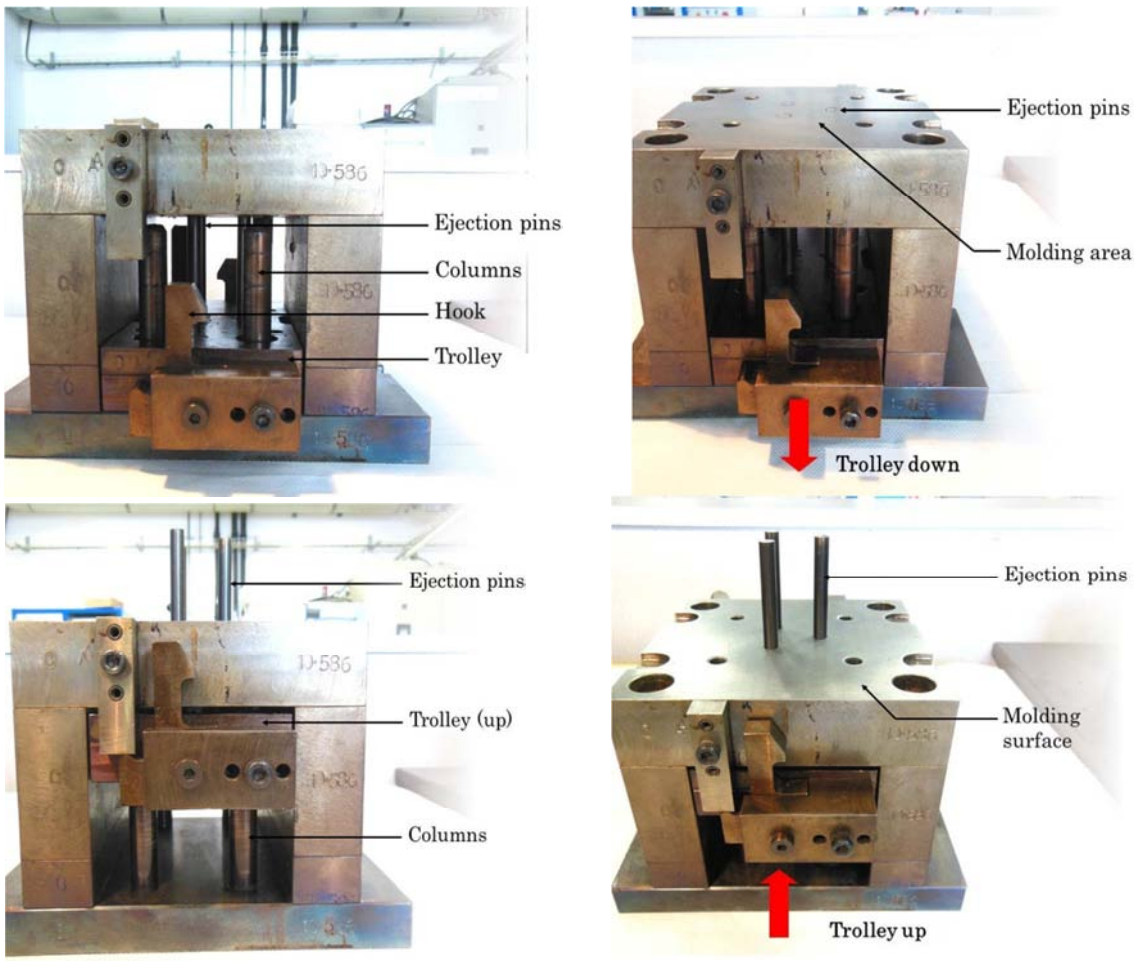


Figure II - 6: 2ROP mechanical ejection system

Available systems would also suffer from high pressure and temperature. Therefore special ejection techniques are required for industrial application, a prototype of mechanical ejectors driven by the pressing machine were designed by 2ROP (Revel, France). Figure II - 6 and Figure II - 7 explains its functioning. The bottom of the die has ejectors going through connected to a trolley that can moves up and down, driving the ejectors through the molding area.

With the die on, the ejectors are down for the molding phase, material is filled and compaction can begin. As the upper part of the mold (punch holder) goes down, a hook connects to the trolley. Upon opening the pressing machine, the trolley goes up with the upper part until a stop disconnects the hook releasing the upper part and letting the trolley up with the part accessible for removing.

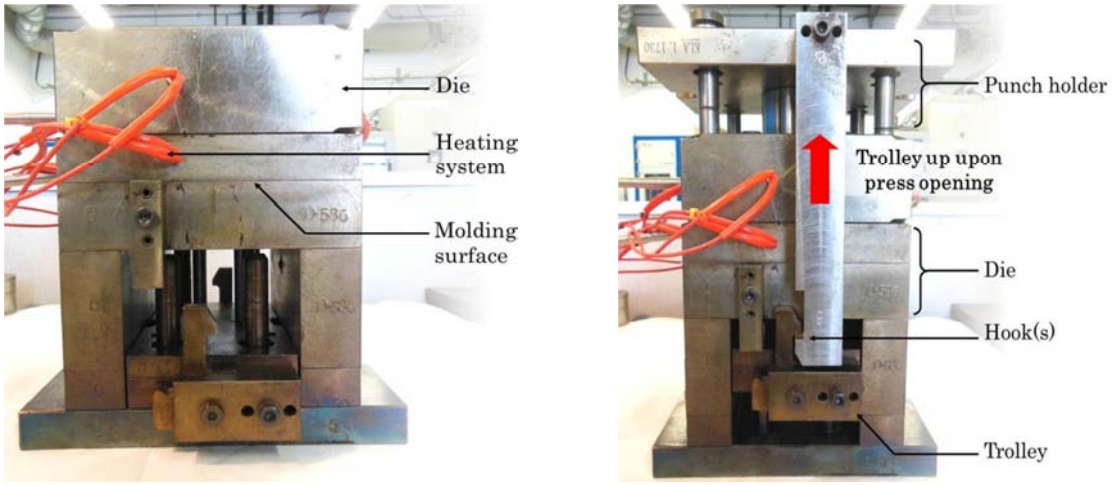


Figure II - 7: 2ROP mechanical ejection system (full setup)

The system works perfectly but long time reliability remains uncertain, notably because of the direct metal-metal friction of ejectors parts through the mold.

II.3.C Homogeneous filling of the mold cavity

The filling of the mold has been a constant source of concern: for example in 2 dimensions, a homogeneous spreading of the material has to be managed, because density will be directly affected by the local thickness of material filled in the mold. Areas were quantity of material is higher (hills) will be more compacted as a result of pressure applied only on part of the surface, thus less compaction on areas were quantity of material is lower (valleys), creating weak points of lower densities.

An experiment was carried out in order to verify the impact of the heterogeneous filling on the mechanical properties of 2D compaction-molded specimens: A first set of dog bone specimens were molded in the control conditions, i.e. manually filling the mold as well as possible, and a second was molded with a 6 mm metal cylinder in the center of the mold during the filing step and normal equalization of the material in the mold. The bar was removed and a normal press cycle was run (Figure II - 8) which created a lower density weak spot (Figure II - 9).

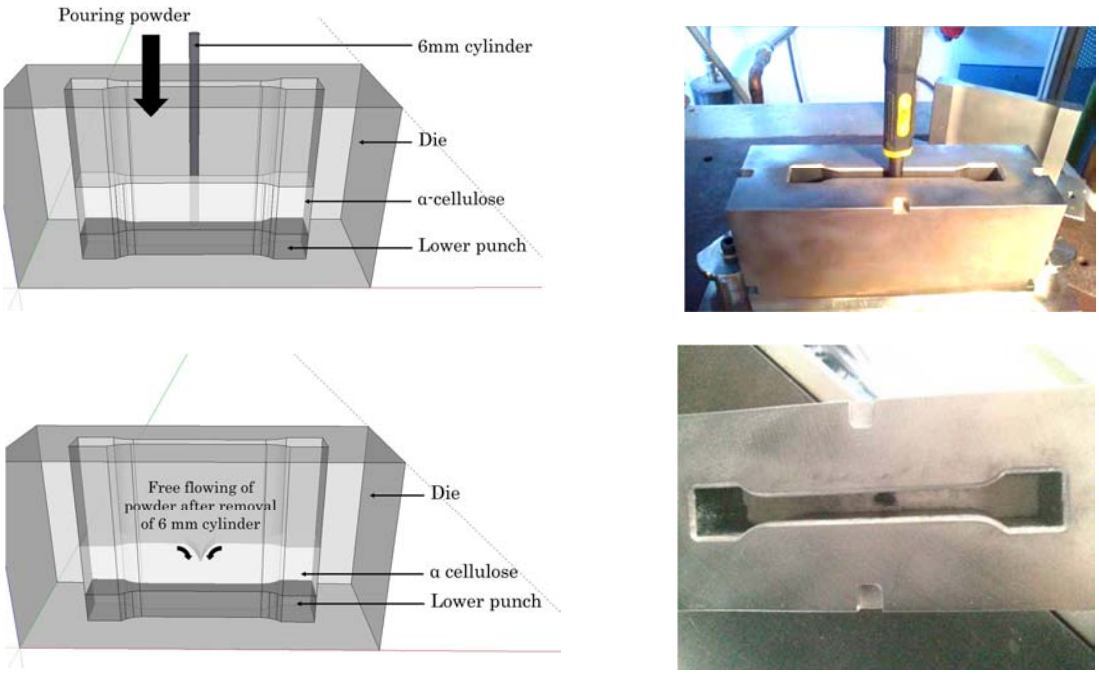


Figure II - 8: Forced heterogeneity of filling experiment

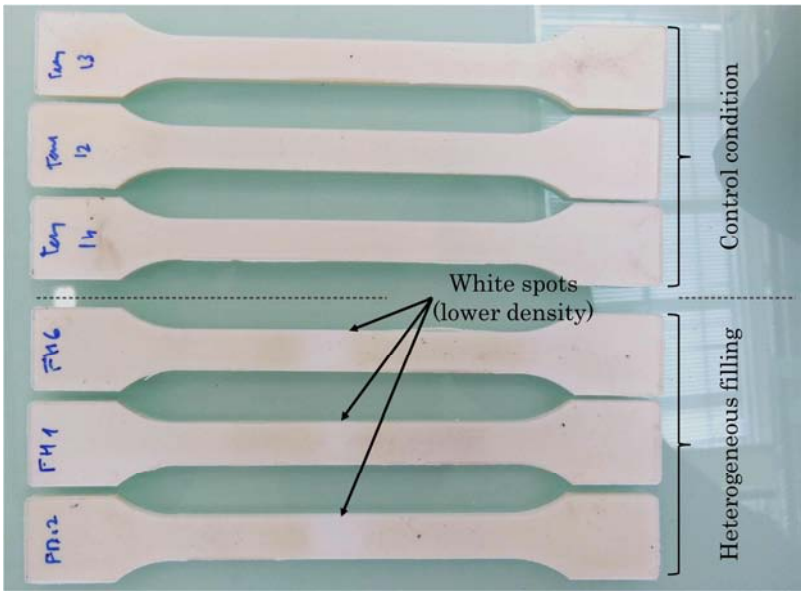


Figure II - 9: Weak spot (whiter) in the centre of dog-bone compacted in forced heterogeneity experiment

Table II - 1: Properties of specimens obtained with forced heterogeneity compared to control

	Thickness (mm)		Bending stress at break (MPa)		Bending modulus (GPa)		Tensile strength at break (MPa)		Tensile modulus (GPa)	
	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.
Control	2.73	0.10	35.9	3.6	5.25	0.41	15.5	2.2	1.45	0.12
Heterogeneity	2.71	0.08	5.8	3.9	2.49	1.03	2.0	1.3	1.37	0.62

As seen on Table II - 1, the stresses at break (bending and tensile) are tremendously reduced when heterogeneity was provoked. On the other hand, the moduli are not that much affected showing that the heterogeneity will affect the stresses at break more than the moduli.

Even if great attention was paid to filling the mold as homogeneously as possible, mechanical properties (especially strengths at break) would be greatly affected by filling. Some trials were made in this sense:

- A vibrating table available in the laboratory was used but the rotational movement of the vibration due to the camshaft construction of the apparatus led to the accumulation of the material on one side. Making the mold rotate on the surface of the table was improving the spreading but the irregularities remained due to compaction in the same way than in a tap density apparatus. Temperature decrease during the vibration step was also inevitable.
- Another setup was made in order to hold the lower punch about the thickness of the non-compacted powder, poor the powder in excess in the mold and sweep the excess on surface of the die. Results were not satisfactory as differences of density (bundles) already exist in the powder which conducted to irregularities. This setup was also quite heavy to use and processing time considerably increased.
- Magnesium stearate was evaluated as a powder lubricant which is commonplace in pharmaceutical tablet production, but this trial conducted to the destruction of the first 1A dog-bone mold, with a lot of material flowing between the punches and die which conducted to the blockade of the mold and seizing while opening.

In order to compensate with inevitable heterogeneities, at least 7 repetitions were performed in tensile and bending in order to compensate with uncertain reproducibility and obtain a more reliable evaluation of the mechanical properties. As can be seen on Figure II - 10, homogeneous filling was even more difficult to obtain when molding parts of larger surface area. When specimens presented exterior signs of heterogeneity, they were excluded from the tests.

Figure II - 10: 2D 5x5 plates made from α-cellulose, heterogeneities can be observed even though great attention was paid while filling

II.3.D Mold filling and flow behavior

In 3D, it becomes quite hard to spread the material with a pattern corresponding to the future part. For example, to mold a bowl with its foot, the center of the molded part were the foot is located contains more material therefore it can be assumed that more material has to be loaded in the center of the mold prior to molding. These ideal patterns of filling are impossible to achieve, first because any manual manipulation of the starting material tend to increase apparent density when grabbing it, shoveling, leveling etc. but also due to the free flowing of powders or particles. Hopefully, molded parts were successfully molded without

matching the ideal patterns because some flow (extrusion) does occur under pressure to correct heterogeneous filling. The flowability of the material during compaction molding is very important and depending on pressure, temperature, material, extrusion occurs (Miki et al. 2003; Takahashi et al. 2009). This allows for instance to mold the edge of the "candle holder" (Figure II - 11).

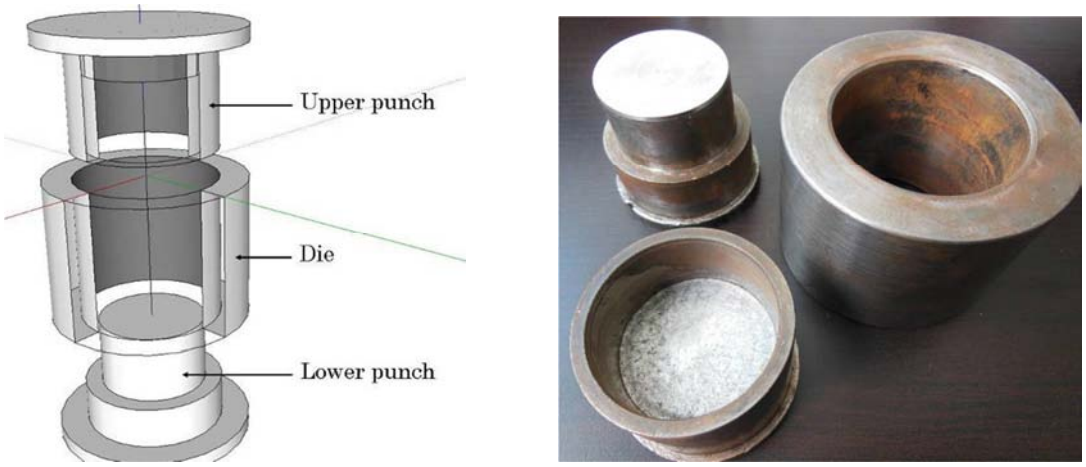


Figure II - 11: Candle holder mold (3 parts)

Molded parts were produced, but heterogeneity was observed, on the edges of the candle holder, like if components of the fibers were separated by compression during flow. The top of the edge of the candle holder (on the bottom of Figure II - 12) is much thicker and darker than the rest of the part, showing that first densification occurred first in this part and secondly flow occurred which formed the edges and bottom of the part (Figure II - 13). A close experiment called "backward extrusion" was reported in the literature in order to evaluate the flowability of wood powders (Miki et al. 2003).

Figure II - 12: Candle holder where lines materializes the flow on the edge of the part

This flow behavior during compaction is complicated to describe, it depends on mold shape, starting materials parameters, molding conditions etc. Here appears another limit of this molding technic: the shape of the molded part is a very important parameter to consider because of flowability in one hand, and possibility of homogeneous filling of starting material in the mold.

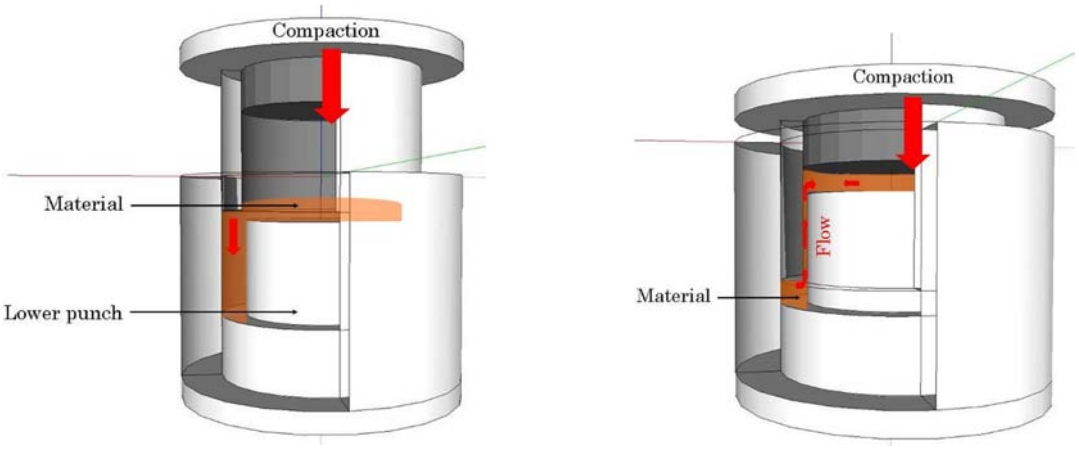


Figure II - 13: Hypothesis of flow behaviour in 3D molding

For instance, when material with poor flow properties are used like α-cellulose, limits of molding are rapidly reached. As seen on Figure II - 14 a color limit could be observed which was concluded to be the sign of not enough compaction on the lighter part due to insufficient flow.

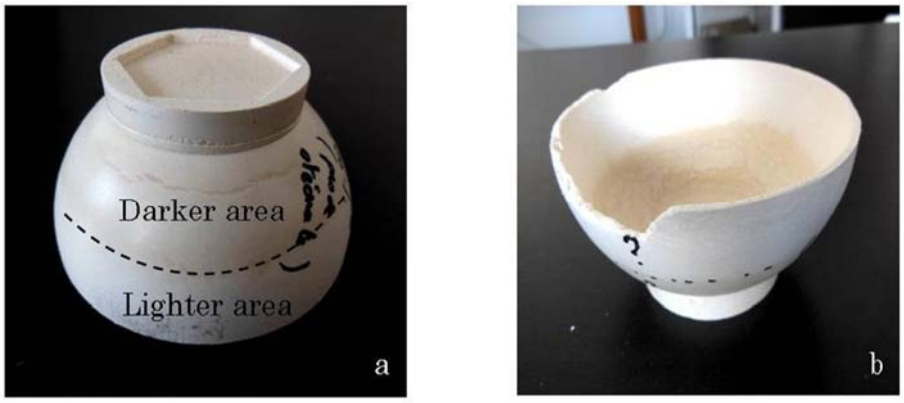


Figure II - 14: Flowability limitation observed on α-cellulose bowl

In fact, in order to mold the 90° part (parallel to compaction force), flow is necessary to transmit the efforts of compaction from the bottom (full compaction – perpendicular to compaction force) to the edges. Depending on materials and conditions the results were different. These observations conducted to the conclusion that a study on the flow behavior of materials was necessary.

II.3.E Steam explosion, delamination

Another very limiting phenomenon during this work was steam delamination: under pressure, water is set free from the plant material because of cells destructuration, densification, hydrogen bonding etc. and remains on the liquid state (subcritical state) under high pressure and temperature. But, at the end of the molding step the pressure is decreased and the free water turns to vapor state and expands, creating pressure and escaping the mold, sometimes causing only minor defects on molded parts, but on extreme conditions the parts can explode when the mold is opened. There is a temperature gradient in the molded

parts (Bouajila et al. 2005). On the surface of the molded part is the highest temperature (mold temperature) and in the inner parts is a lower temperature zone thus water content will be higher inside the material as can be seen on Figure II - 15, and vapor pressure upon demolding will be maximum in the inner layers of the molded material.

Figure II - 15: The two parts of a compaction-molded miscanthus specimen, violent delamination occurred, the centre of the material was observed to be darker due to moisture accumulation

Of course, depending on composition, material condition (moisture, granulometry etc.), molding parameters, shape of the mold, the delamination was different, occurred under different conditions, on different places of a molded part outside from the same mold etc. In the first time, trials were performed in order to minimize steam delamination which did not give satisfactory results, mostly because mechanical properties and/or flowability were also affected.

Figure II - 16: Different plant materials compacted in the same conditions, only some suffered from delamination (175°C – eq. 60% RH – 200 MPa – 30 seconds)

Everything was occurring as if the steam delamination was a compulsory drawback resulting of the expression of flowability and mechanical properties. Whatever the material, satisfactory 3D shapes were obtained in the conditions that heavy steam was generated in

the mold conducted to cracks in the part, and poor flowability and fragile edge were obtained in conditions designed to prevent steam delamination.

When conditions are optimal for strength and flowability, a good surface effect is obtained (plastic-like, shiny and smooth) that vapor cannot penetrate easily. Thus, best conditions of molding are precisely those for which molded parts experience delamination. Once broken due to pressure, and because of compaction, the material acts as a gasket and the punch part of molds are pushed by the steam pressure when the press is opened. In extreme cases, the punch can be ejected from the mold by the steam pressure (Figure II - 17).

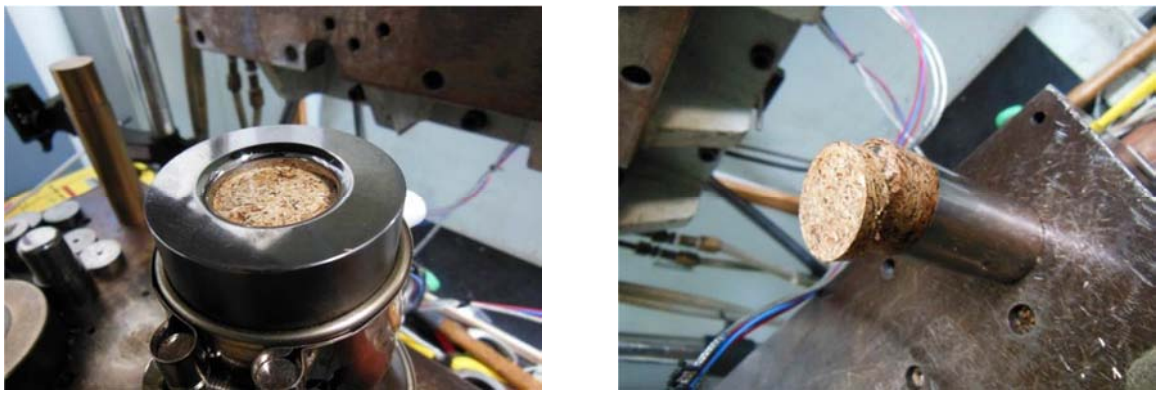


Figure II - 17: Steam delamination phenomenon and gasket effect - pictures

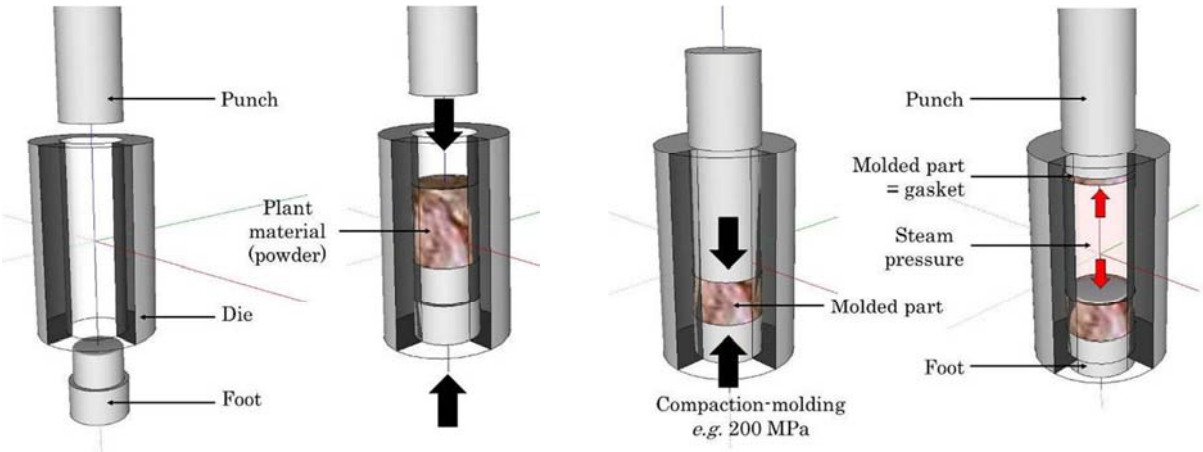


Figure II - 18: Steam delamination phenomenon and gasket effect – interpretation

On Figure II - 17, on the left is the upper part of the molded object that has been pushed by steam pressure all on top of the die (about 8 cm), on the right, the result of the molding: the part is broken in two in the transition zone between the bottom of the small pot and its edges.

In some cases, it is possible of course to release the pressure very slowly, which reduces the damages on the molded parts, but a crack is observed, where in normal condition, a crack would have opened as a result of delamination. The same result was obtained if the mold is let to cool down completely under pressure before releasing it: a weak line remains on the delamination point. Besides, for industrial application, such a cooling step would be so energy and time consuming that this option was excluded from the study.

II.3.F Shear and steam explosion

The molded pieces area where steam delamination occurred is a quite interesting point to mention: it was observed that delamination always occurred in shear transition zones. For instance, on the bowl shape (Figure II - 19), steam explosion occurred on the transition from the foot to the bowl. Also on these points, constituents' separation was observed, darker color, very shiny surfaces showing that some constituents (lignin?) were extracted and concentrated on these high shear points. Probably, water also accumulates were shear is maximum, as a result of cell destructuration. Thereafter, trials were performed in order to find a compromise between flow which produced strong and completely molded parts (hard conditions) and the avoidance of delamination (gentle conditions). It seems a compromise is hard to find, depends on the starting material, operating conditions, but most of all, if steam delamination is avoided, the edges of the bowl are less shiny, weaker which showed that flow was insufficient for the pressure to be transmitted to the edges. The shape of the mold probably also plays an important role.

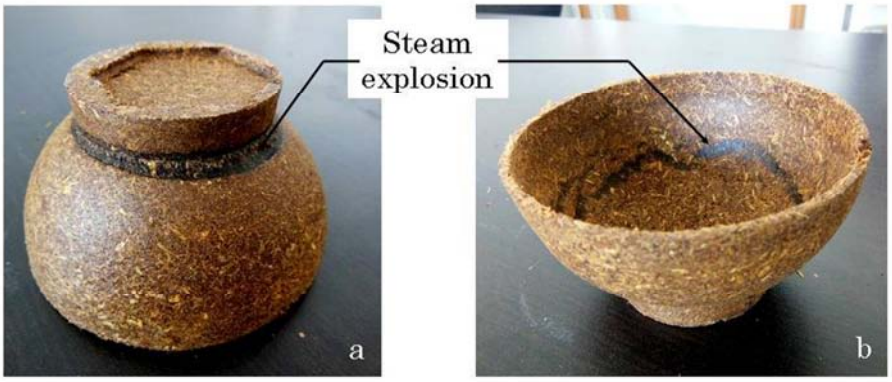


Figure II - 19: Slight steam delamination occurring on bowl (pressure was released slowly)

II.4 Transfer molding

II.4.A Principle

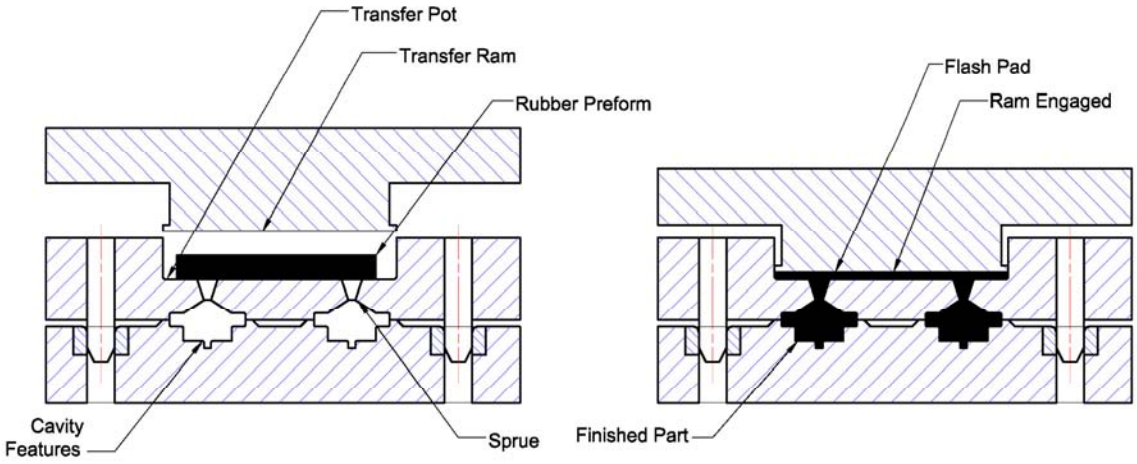


Figure II - 20: Transfer molding for rubber molded objects production (reproduced from twistertechnology.com/)

Transfer molding is industrially used for processing non melting polymers like rubber, PTFE etc. The principle is to force the starting material in a chamber that flows out on exits (dies or sprue) to fill a mold cavity (Figure II - 20).

This technique relies on a certain ability of the material to flow through the die to fill a cavity which relies on the same principle that a capillary rheometer to evaluate the flowability of materials under pressure (Takahashi et al. 2009). Concerning plant fibers molding, the group of Kanayama et al. in Nagoya has been pioneer in designing an apparatus to process bamboo and wood powders using transfer molding (Yamashita et al. 2007).

II.4.B Advantages over compaction molding and drawbacks

Transfer molding has no shape limitation due to its design like compaction molding and thus can produce much more complicated shapes (Figure II - 21). Transfer molds can be designed like injection molds for which there is much more knowledge; the industrialization also would probably be much easier. As the material is preloaded in the compression chamber there is less concern in filling the mold homogeneously. Also, the same compression chamber can be used with different molds, which means that only this part will suffer from friction and damages.

Figure II - 21: Examples of complicated shapes obtained by transfer molding

II.5 Other technical locks

II.5.A Moisture adjustment

The effect of moisture is quite important, thus, moisture adjustment is necessary and uncertainties on moisture content are rapidly occurring. A precise control of moisture is quite difficult, as it requires climatic chambers to adjust moisture, or a precisely controlled partial drying of one material, but most of the difficulty came from the processing steps which obligatorily takes place in room conditions: the starting materials was charged in a hot mold and leveling could take a few seconds, and not always the exact same time which will undoubtedly modify the moisture content and generate some heterogeneity in the results.

II.5.B Particle size

Due to the size of molded objects studied in this work, both techniques required grinding steps which is energy consuming, and raises problems about particle size and distribution and their effects on the molding. Within one batch, heterogeneity was also possible from a specimen to another even though mixing was performed at regular intervals.

II.5.C Machining, thermal dilatation and seizing of molds

Compaction molding and transfer molding both require a lot of pressure for the material to be molded or flow correctly. As temperature was a crucial parameter to evaluate, molding tests were performed from room temperature to 250°C. One very difficult part was the design of the molds. They should be as tight as possible in order to prevent the material from being extruded between the punch and die, but due to metal dilatation with heat, a minimum of slack is needed. When the slack is not enough, seizing occurs, as can be seen e.g. on Figure II - 22. The 2ROP mold was designed with columns and metal was 40CMD8 which is a pre-treated alloy steel capable of 110 - 120 kg/mm². This mold was designed like an injection mold for which the manufacturer is an expert, but too little slack rapidly conducted to seizing on the punch and die. The lack of guiding was not involved because of the presence of 4 guiding columns on this mold. Later trials were made on the 1A dog-bone specimen mold machined by CEE (Grisolles, France) on a stronger alloy (55NCDV7 – 140 to 150 kg/mm²). Mechanical slacks from 3 to 6 µm face to face were tested. 3 µm slack conducted to a very tight mold, but seizing occurred after about 100 cycles. 6 µm slack permitted to mold many more specimens, but when testing material with better flowability, 2 molds were broken by extrusion of the material between punch and die, which, during the removal of the punch from the die conducted to seizing. When seizing initiation was detected, sanding paper was used to smoothen the surface, but then inevitably the slack was increased and soon or later, the mold will tend to be blocked by extruded material.

Figure II - 22: Seizing marks on 2ROP mold (columns guided mold)

The use of alloys with different strength was also tested on the 4th version of the 1A dog-bone specimen mold, which, associated with a treatment on the punch conducted to good results. To date, the understanding of these phenomena remains quite unclear and much work is still needed on the technological part.

III Study on a model polymer: α-cellulose

The processing of cellulose into solid materials have been of raising interest these last decades, generating a lot of scientific papers and ending up with a wide variety of processing routes. This chapter will begin by a quick review over the different techniques. This thesis focused on thermo-compression molding, which have been less studied, for its simplicity and assumed eco-compatibility.

As seen in the literature on binderless thermo-compressed plant materials (Chapter I), cohesion is often associated with hemicelluloses and lignin, or free sugars, starch and proteins if present in the starting plant materials. Binderless molding of pure cellulose have been very rarely reported; and one of the first formulated hypothesis was that cellulose could not pretend to any self-bonding ability without being modified, solubilized or processed in the wet state. At first, cellulose was chosen as a "negative control" model polymer, i.e. with the idea that low mechanical properties would probably be obtained, and that using materials with hemicelluloses and lignin will conduct to higher properties. As will be seen in this chapter, there was much more to study about the thermo-compression molding of cellulose than expected. Surprising features of the compressed cellulose specimens were discovered all along the thesis, and what was expected to be a 3 months short study with lot of negative results ended up to take most of the experiment time in this thesis.

The first available mold at the beginning of this work was the 50 x 50 mm square. First results were obtained by cutting the squares in 5 small test specimens of roughly 10 x 50 mm. High scattering was observed, but some specimens were incredibly strong. In order to avoid the cutting step and to reduce the dispersion of the values, it was decided to design a mold that will allow the molding of 1 specimen per cycle. As the tensile properties were never reported on compression-molded cellulose samples, a dog-bone mold was machined which will allow both tensile and bending tests.

A first step was to validate the method: it was rapidly observed that the filling of the mold was an important parameter that will generate a bit of dispersion on the values (see Chapter II). But there was no comparison with what was obtained from cutting samples out of a 50x50 square. In order to evaluate correctly the mechanical properties, 7 repetitions were performed on each modality, and the effect of the different molding parameters could begin. The first results concerned a first evaluation of the parameters and were published (Pintiaux et al. 2013).

Additional data were produced later, when studying the effect of lower pressure and the conjugated effect of reduced moisture and increased temperature on delamination phenomenon and on the mechanical properties of the specimens.

In parallel to this, some data were collected towards the understanding of the physico-chemical phenomena occurring during the consolidation process. Also, because the interest of 3D molding was high, flow tests were performed thanks to a JSPS internship in Nagoya Japan.

III.1 The different ways to process cellulose into solid material

III.1.A Native cellulose structure

Cellulose is a linear polymer of ß1-4 ether linked glucose. The DP can be as high as 10000 units in common plants, and more in micro-organisms. Molecular chains are assembled in parallel held by a complex hydrogen bonding network which forms crystalline structures. Two crystals allomorphs I_α and $I_ß$ exist in the native cellulose and coexists with some paracrystalline and amorphous cellulose (Nishiyama et al. 2003).

Cellulose in plants has a fractal-type organization. The assembly of several side chains builds up nano-fibrils of a few nm wide. There are evidences of the existence of an elementary unit (CEF: cellulose elementary fiber) of 3.5 nm of diameter which would

integrate 36 adjacent cellulose chains in a diamond like cross sectional organization (Somerville 2006). The CEF are auto-assembled in higher scale structures of approximately 20 to 35 nm wide, which are called micro-fibrils. The distinction between the nano-fibrils and micro-fibrils is quite recent (Chinga-Carrasco 2011) and nano-fibril has more a technological meaning (Figure III - 1). The term micro-fibrils used to described the two of them in the past, with typical sizes reported in a quite large range from 1 to 50 nm which has been a source of debate (Ohad and Danon 1964) that is still not completely elucidated.

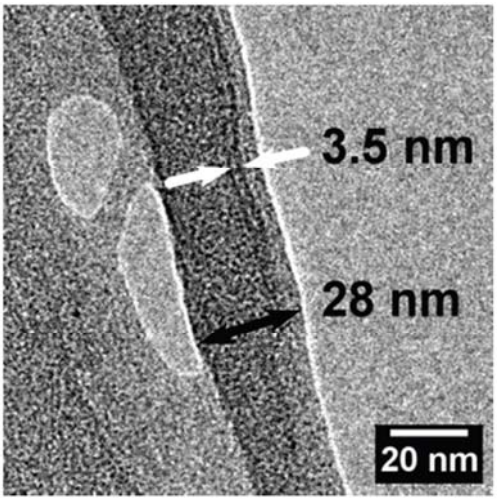


Figure III - 1: TEM picture of a nano-fibril cellulose micro (white arrow) composing a micro-fibril (black arrow), (reproduced from Chinga-Carrasco 2011)

The micro-fibrils together with other components such as hemicelluloses, lignin, pectins, proteins etc. are sometimes reported to be assembled in higher structures called fibrils (or macro-fibrils). The size of the macro-fibrils (20 to 100 nm wide) varies upon species and cell-types (Donaldson 2007) and it remains a rather vague notion that is sometimes mistaken, because the elementary fiber (CEF) is sometimes called micro-fibril and thus micro-fibrils called macro-fibrils (Mellerowicz et al. 2008). The micro-fibrils, these elements composed of several CEF are the "frame" part of a nano-composite material of extreme complexity and performance: the plant cell wall (Figure III - 2).

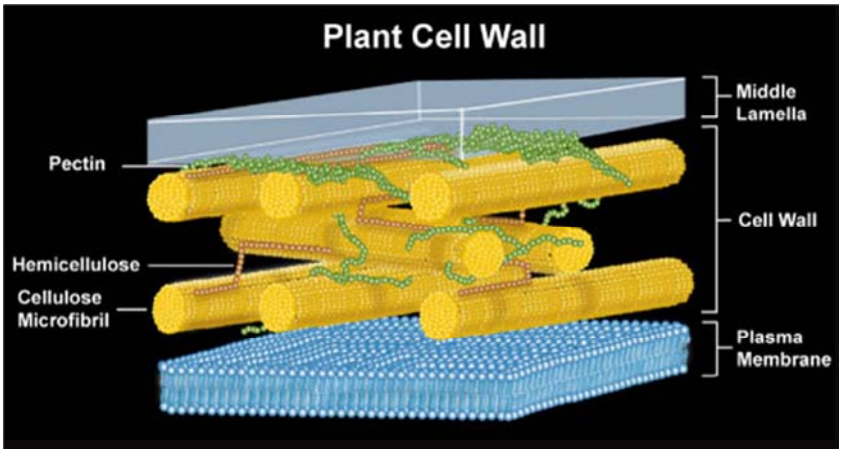


Figure III - 2: Plant cell wall constituents' super organization, reproduced from sigmaaldrich.com

The cell wall is specific to the plant kingdom, and it lies against (or around) the plasma membrane, that is the main cell's barrier of any living organism. The plant cell wall is described as a layered structure, comprising, from the inside to the outside, first the S3, S2, S1 layers of the secondary wall, the primary wall, and finally the middle lamella which is a matrix-like component that forms the "cement" between adjacent cell walls (Figure III - 3). During the cell's growth, the primary wall is the only present, it is soft and grows, deforms, with the cell, but when the rigid secondary wall is synthetized, the cell's growth stops.

These layers also have different constitution, for instance, in wood, the primary cell wall is mostly constituted of cellulose pectin and hemicelluloses while the secondary wall is made of cellulose hemicelluloses and lignin like the middle lamella that rich in lignin, pectin and proteins. Depending on plant origin, the organization can differ a little (Ding et al. 2014). The S1, S2, S3 distinction also takes place in the different orientations of the cellulose fibrils (Figure III - 4), which gives to the plant cell wall a particular strength, necessary to handle the turgor pressure (turgidity).

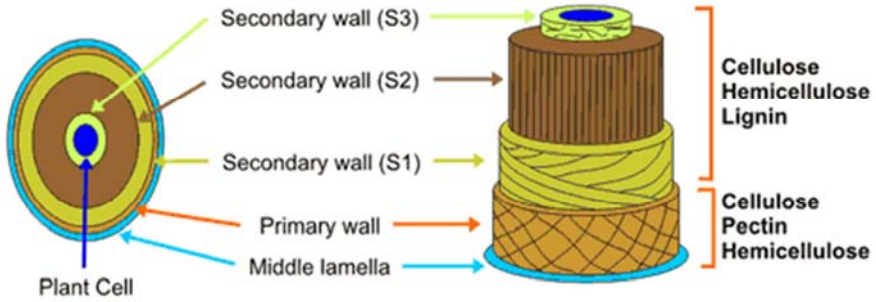


Figure III - 3: Plant cell-wall super-organization, reproduced from bioenergy.ccrc.uga.edu

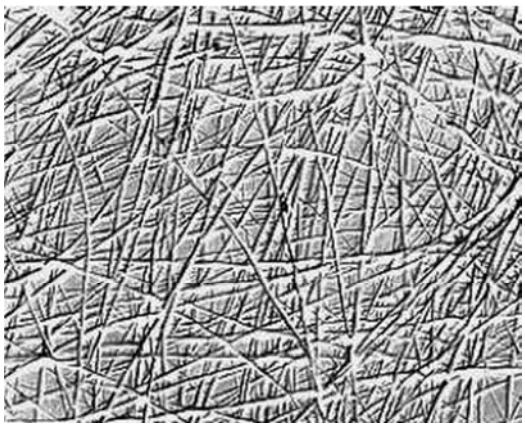


Figure III - 4: Differently oriented cellulose microfibrils in the cell wall (TEM picture, X 30000) reproduced from acces.ens-lyon.fr

The cell wall forms a rigid 3D structure that is called "fiber". In the living plant, the fibers in fact refer to individual cells, which, once they have been extracted are hollow structures of about 20-50 µm wide and about 1 mm long. "Cellulose fibers" can be produced by removal of other components than cellulose (like removing the "cement" and keeping the "frame" intact). This is what can be observed under a SEM of holocellulose, the most basic cellulose extraction out of plant fibers. Holocellulose is prepared from ground plant materials by sodium chloride treatment and filtration which removes lignin and extractives and leaves cellulose and hemicelluloses (Sjöström and Alen 1998). From holocellulose, a 17.5% NaOH

treatment dissolves most of the hemicelluloses (and some of the cellulose) which produces α-cellulose after filtration (α by opposition to ß which was the dissolved part that could precipitate upon acidification and γ the part that is lost and does not precipitate). Today, α-cellulose has the signification of its processing route and the original meaning of the "α" is quite out-dated.

A mild acidic treatment run on α-cellulose will hydrolyze the rest of the pentosans from hemicelluloses and part of the cellulose, beginning with the less stable and most accessible parts of cellulose: the amorphous phase. This will produce micro crystalline cellulose, a pure cellulose material with significantly lower DP than α-cellulose, with increased crystallinity index and wherein the fiber's shape is partially lost due to hydrolysis.

III.1.B Cellulose polymer basic properties

Paracrystalline organization

Cellulose is considered a semi-crystalline polymer, i.e. it comprises crystallites and amorphous phase. Yet, the classic semi-crystalline model originated from synthetic polymers does not fit very well to cellulose. For instance the amorphous phase of cellulose has very vague properties and it is more adequate to consider a crystalline, paracrystalline and amorphous phase, i.e. a paracrystalline model. The paracrystalline phase is reported as a thin mono-molecular layer on the surface of crystals (Ioelovich et al. 2010). The amorphous phase would then be surrounding the paracrystalline phase but its characteristics are still unclear. The natural cellulose crystal are under the I form. Cellulose Iα is majorly found in bacteria and algae while Iß is majorly occurring in plants. Cellulose Iα crystals have a parallel single chain triclinic organization although Iß is two chains monoclinic. Cellulose II which is the form obtained upon mercerization or regeneration of cellulose (Viscose, Lyocell etc.) has an antiparallel two chains monoclinic organization. Cellulose II is thermodynamically more stable than the Cellulose I allomorphs. These are the most current allomorphs, but others can be obtained by chemical treatments (Figure III - 5).

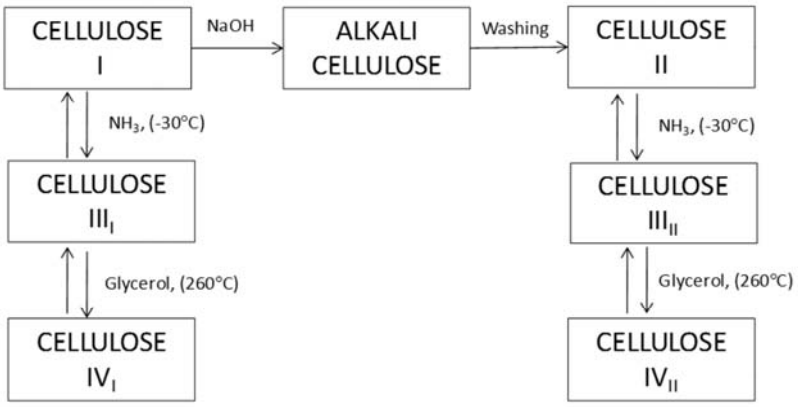


Figure III - 5: The different cellulose allomorphs

Fusion temperature

There is no fusion temperature (Tf) of cellulose, since the energy needed for freeing the polymers is too high and lead to the degradation of the polymer before it melts. However, in very particular conditions (i.e. uniaxial pressure, mechanical shear and short high energy laser beam exposures), the melting of cellulose has been reported (Schroeter and Felix 2005).

Glass transition temperature

The existence of the amorphous phase in cellulose is long time considered, and thus the research of a glass transition temperature has been for a long time under discussion. The glass transition temperature is a feature of a semi crystalline polymer that concerns the amorphous phase. At temperatures under the Tg, the amorphous phase is under the glassy state which confers low or no molecular motion ability. At and after the Tg, some molecular motion is obtained, and the amorphous phase switches to the rubbery state with higher molecular motion and deformability.

In the field of paper processing, the Tg of cellulose seems almost "classical": the Tg of paper is announced at 47 to 67 °C in modern technical books (Ashby 2012) which refers to mechanical properties of paper and a particular interpretation. More generally, the Tg of cellulose has been constantly discussed by chemist among the decades. It was measured around 220°C in the dry state (Back 1987). Values of 230 – 250°C have been found by RMN measurements based on bound water evaluation (Ogiwara et al. 1970). More recently, studies appeared with very low values of Tg reported (Szcześniak et al. 2008). These measurements using DSC are not very reliable and the peak can hardly been observed. Measurements base on DMA of powder have concluded to more reasonable values (Paes et al. 2010).

Thermal decomposition

Thermo-gravimetric analysis of α-cellulose showed that the degradation of cellulose starts around 230 – 240°C in both air and nitrogen conditions.

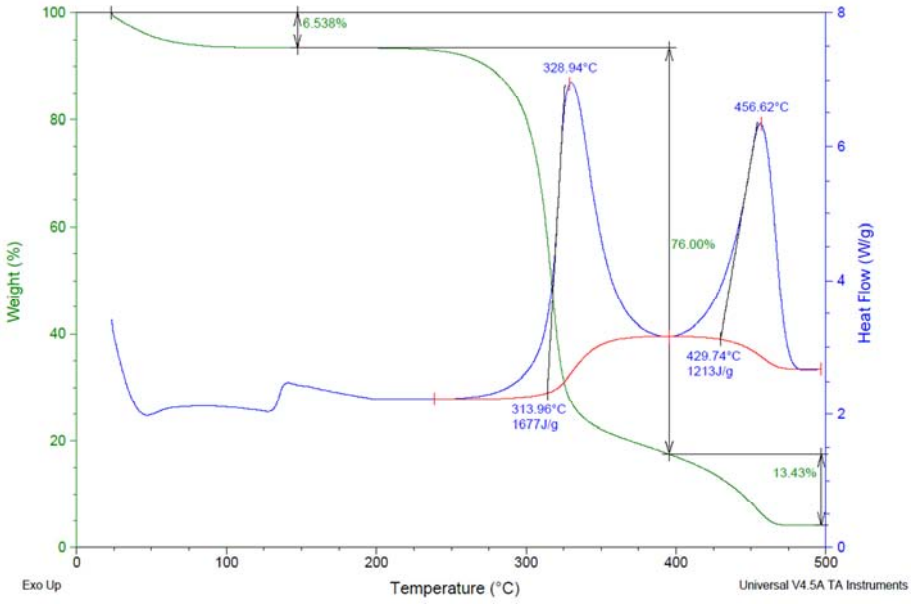


Figure III - 6: DSC-TGA of α-cellulose under air condition

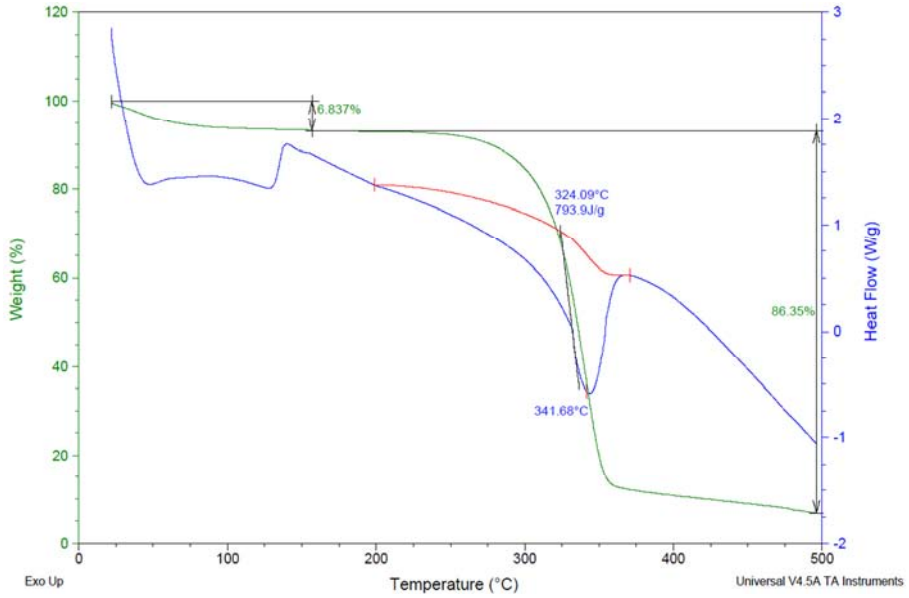


Figure III - 7: DSC-TGA of α-cellulose under inert (nitrogen) condition

These analyses that are run under atmospheric pressure does not inform about the degradation of temperature of cellulose under pressure, for what very few reports have been published. The possible hydrolysis of cellulose in sub-critical water under a pressure of 25 MPa and temperature range from 290 to 400°C has been mentioned (Sasaki et al. 1998) which is probably compatible with the molding conditions used in this thesis work.

III.1.C Cellulose to solid materials processing routes

Paper and other water suspension processes

The first historic example was invented in China short before J.C. The modern paper area started around 1825 with the widened use of paper machines. Paper is based on the transformation of plant materials into "paper pulp". Chemo-mechanical processes are used to break down the plant-cell wall assembly, make the fibers (plant cells) swell in a water suspension, separate from each other and intertwine. Although many plant materials can be used, the properties of paper are highly impacted by the length and strength of the fibers. Hemp or linen can be used, but wood is nowadays the preferred starting material for pulping. Softwood and other low density woods which have longer fibers are preferred to produce paper which will require a certain strength like newspaper that are printed in high speed rolling printing presses.

The pulping process aims at separating the fibers one from the others and hydrate the fibers by felting their surface (fibrillation) in order to increase the surface area for better water access. The link between a type of pulp and a type of paper is tight. Several processes of pulping co-exist, depending on the desired pulp and paper. Chemical pulping and mechanical pulping are the two main processes which for many variants actually exist:

* Chemical pulps are the most produced pulp worldwide, chemical dissolution of the middle lamella (lignin) is performed using either an acidic treatment (bisulfite) or alkali (soda, sodium sulfur) for which the Kraft process is a well-known example. These types of pulp achieve the best cellulose purity (and lowest yield) and produce the less damaged fibers.
* Mechanical pulps using either defibering techniques (abrasion of the debarked wood logs) to strip fibers off which produce a type of pulp known as SGW (Stone Ground Wood) or refining of pre-ground wood chips using disks or cones refiners which produce RMP (Refined

Mechanical Pulp). The refining produces higher quality pulp with longer fibers than the defibering techniques. Mechanical pulping has a high yield over 90%. Thermomechanical pulp is a variant which is characterized by an extra steam pretreatment of the wood chips before being refined.

Most of today's pulping processes combine mechanical and chemical processes. These processes starts with wood chips being treated with chemicals (alkali and sodium sulfite), possibly under steam pressure and proceed further to mechanical refining. The color of the pulp (thus of the paper) is adjusted by a final bleaching step which deals with the removal of the colored lignin elements using oxidizing (hydrogen peroxide) or reducing agents (sodium hydrosulfite). The adjustment of the different parameters on these different steps allows to produce a high variety of pulps, with various cellulose content, strength, optical properties, etc. For instance, highly chemically treated pulps are used to produce newsprint and glossy papers while more mechanically treated pulps will give printing / writing papers.

Related products based on the same phenomena (water suspension process) are numerous: cardboard, papier mâché, egg boxes-type products and more recently materials based on fibrillated cellulose. The fibrillated celluloses are a quite recent development of the paper process, which relies on the refining performed on a higher extent by the separation of smaller elements at a scale between the fiber and the elementary fiber. High pressure homogenizer treatment has been a preferred route for producing micro-fibrillated cellulose (Turbak et al. 1983). MFC is not a very strict denomination, as commercial MFC contains a range of cellulose elements size from the fibers to the nanofibril (Chinga-Carrasco 2011). Zelfo is an example of MFC that is produced using processing tools which are used in the paper industry and under development for producing solid material by spraying or press-wringing processes. Zelfo technology (the company that now possesses the Zelfo patents) recently found applications in the reinforcement of cardboards (Lavoine et al. 2014).

The bonding ability of MFC depends directly on the degree of refining, i.e. the separation of the fibers into thinner elements. The group of Yano et al. produced a micro fibrillated cellulose with nanometer web like network using a repeated (up to 30 times) high pressure homogenizer treatment to produce a hot pressed material with 16 GPa of bending modulus and 250 MPa of bending strength at break (Yano and Nakahara 2004). Another technique based on a water grinding treatment was designed by this research group and hot-pressed into solid material with a reported Young's modulus of 8 GPa and 90 MPa of ultimate stress at break. The process was reported to produce nanofibers with uniform width of 15 nm (Abe et al. 2007). The fundamental difference between these works and Zelfo / MFC is the degree of refining, which came from micro to nano scale.

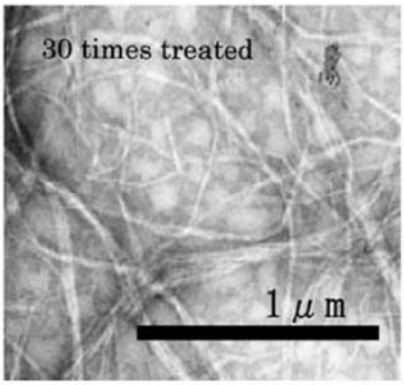


Figure III - 8: "Cellulose microfibers with nanometer unit web like network" also called "microfibrillated cellulose" in the pioneer work of Yano, before the first usage of nanofibrillated cellulose (Yano and Nakahara 2004)

The modern science infatuation for nano objects rapidly led to name "nano-fibrillated cellulose" (NFC) the slurry obtained by cellulose refined to a higher degree than MFC. However, the definition of nano-fibrillated cellulose remains vague, most of all because if confuses with the definition of nanofibrils (the elementary fibrils of 3.5 nm). A pragmatic (technological) characteristic of the elements' size reduction was to obtain so called "nanopapers" with much higher mechanical strength (214 MPa according to Henriksson et al. 2008) and optical transparency. The group of Yano which were pioneers in this way presented a transparent NFC sheet with a Young's modulus 13 GPa and a tensile strength of 223 MPa claiming an enormous potential for industrial applications (Nogi et al. 2009).

Another approach that is based on the same concept for material's cohesion but on a different way for obtaining the nano fibrillated cellulose was found with bacterial cellulose: when microorganisms (for instance Acetobacter aceti) are grown in water adding nutrients, a network of cellulose nanofibers is grown, which gives a slurry wherein solid if 97% α-cellulose after purification (Yamanaka et al. 1989). Films were obtained by casting, and DMA analysis conducted to a Young's modulus of 18.8 GPa and a tensile strength of 260 MPa.

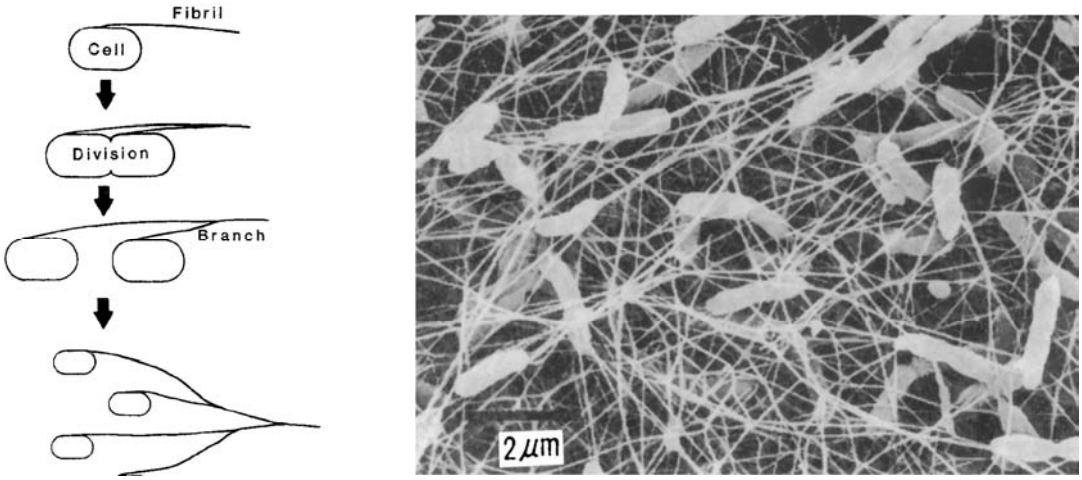


Figure III - 9: Bacterial cellulose (wires) and bacteria, synthesis scheme on the left reproduced from (Yamanaka et al. 1989) and SEM picture on the right reproduced from (Iguchi et al. 2000)

Solubilization process

Nitrocellulose (1855) was the first semi-synthetic polymer produced from cellulose. It was highly flammable which rapidly restricted its use (only Ping-Pong balls are today still made of nitrocellulose because of its unique characteristics). The basic idea was to modify the native cellulose polymer to make it soluble. Shortly after nitrocellulose, cellulose acetate was invented which is still used today. Viscose followed up (1884) and was produced worldwide from 1920 to 1950 when the first synthetic polymers were discovered. The interesting feature of viscose is the fact it is woven from regenerated cellulose, i.e. cellulose that has been dissolved (thanks to modifications involving sodium hydroxide and carbon disulfide) and precipitated. Viscose was a widespread polymer used for textile mainly, and even though the concurrence of synthetic polymers was high, remained under production. This industry produced massive amounts of polluting wastes and was terrible for the workers' health mostly because of carbon disulfite exposure. Health problems led to measures for protecting workers with a 10 ppm maximal exposure limit to CS_2 that is still judged insufficient (Gelbke et al. 2009). Modern alternative solution to viscose appeared in the 1980's (Carbamate cellulose, similar to viscose but CS_2 being replaced by urea) and the 1990's with the

application of NMMO (N-methylmorpholine oxide) as a solvent for cellulose which produced a regenerated cellulose materials without derivatization called Lyocell (Fink et al. 2014).

The question of cellulose's solubilization has been a constant concern of researchers for about hundred years. The newest methods now use the DMAc / LiCl (Dimethylacetamide / lithium chloride) for what recent applications was found for high performances films according to the concepts of "all cellulose composite". The technique relies on a sequential exchange of solvent from water to DMAc through ethanol and acetone and the final addition of LiCl to solubilize cellulose. Depending on the time of contact between cellulose and the solvent system, the extent of the dissolution can be controlled (so-called selective cellulose dissolution). This allows dissolving of only the fibers' surface for obtaining strength but without total solubilization which lowers DP and destroys the advantages of the fibers native structure. The removal of the solvent by rinsing and casting produces very high performance sheets: e.g., Nishino et al. (2004) processed a composite made from pre-oriented ramie fibers and Kraft pulp solubilized cellulose matrix which obtained a dynamic storage modulus of 45 GPa and an amazing tensile strength of 480 MPa. Gindl and Keckes (2005) processed micro-crystalline cellulose the same way and obtained an anisotropic all cellulose film which had 13 GPa of Young's modulus and 243 MPa of tensile strength.

Compaction molding

Cellulose has been used as excipient in the production of pharmaceutical tablets for decades since the discovery of microcrystalline cellulose (Thoorens et al. 2014). The compaction process uses pressure in the same range as employed in this thesis, generally from 100 to 200 MPa. Pressurization speed is however much higher and is in the range of hundreds of mm/s. The process does not really consider a molding time separately from the ram speed, but can imply pre and post compression which acts like an increase of compaction time. An equivalent holding time would be less than a second. The moisture content of the powder is generally low (bellow 3% MC) because water would interfere with the active principle.

The mechanical properties are one of the main concerns of this science; the Young's modulus in elastic uniaxial deformation can be about 10 GPa. Relative porosity is the main parameter that is used to describe the features of the tablets and for the modeling of the compaction process:

$$Relative\ porosity = \frac{Apparent\ tablet\ density}{Absolute\ powder\ density}$$

The apparent tablet density is on the macroscopic point of view. The powder density is measured using an helium picnometer, which for α-cellulose usually gives a value of 1.57 g/cm^3. Jallabert worked on the modeling of the densification process observed in the PVT measurements made at the LCA during his thesis, and it was concluded than the classical pharmaceutical models could not explain the densification observed at elevated temperatures under the conditions of the PVT apparatus (Jallabert et al. 2013).

Other research works have been published recently around the use of compression molding to produce cellulose solid materials:

Nilsson et al. (2010) reported the production of compression molded material from wet cellulose disintegrated pulps using a two-stage (Cold, 7 min, 0.6 MPa/Hot, 20 min,−45 MPa) pressing step, their material reached 11 GPa of Young's modulus and 76 MPa of tensile strength. Also, Rampinelli et al. (2010) studied the mechanical properties of compression molded highly refined micro-fibrillated cellulose. They produced a material with 180 MPa of tensile strength, 165 MPa of bending strength and a bending modulus of 9.4 GPa with an optimized process using 120 MPa of pressure, for 6 min at 160 °C. Also, Zhang et al. (2012) produced ball-milled cellulose material from non-treated cotton linters micro-crystalline

cellulose using a high shear device usually dedicated to the sintering of metals and reported a bending modulus of 1.84 GPa using DMA measurements. Finally, pressures from 700 MPa to 2.5 GPa were used for the compression of cotton linters which led to the destructuration of the original fibers shape to a network of reassembled nanosized elements (Privas et al. 2013).

Table III - 1: Summary of the main processing routes from cellulose to solid materials,

	Product	Product. start	Concept, forming method	Tensile properties*	Energy consum--ption	Pollution	Proces--sing time
Water suspension	Paper	1820	Cellulose pulp press-rolled, dried into sheets of 20 - 120 g/m²	~ 10 - 50 MPa	+	-	-
	Cardboard, paperboard	1850	Less refined, cellulose pulp, much heavier 120 - 300+ g/m²	~30 MPa	+	-	-
	Eggboxes - molded pulp	1900	Pressure-wringing/vacuum forming of papier mache for 3D shape	-	+	-	-
	Zelfo	1997	Fibrillated pulp pressed or molded	6.5 GPa - 55 MPa	+	-	+
	Nanopaper Yano 2004- Nogi 2009	-	Nanofibrillated cellulose casted into transparent films	13 GPa - 223 MPa	++	-	+
	Nanopaper Berglund 2008	-	High strength Nanopaper	214 MPa	++	-	+
	Bacterial cellulose sheets Yamanaka 1989	-	High strength nano cellulose film	18.8 GPa - 260 MPa	-	-	++
Solubilization	Viscose	1920	Regenerated cellulose (NaOH, CS_2)	300 MPa	+	++	-
	Lyocell	1992	Regenerated cellulose (NMMO)		+	+	-
	All-cellulose composite Nishino 2004 (oriented)	-	Partially regenerated cellulose (DMAc LiCl)	45 GPa - 480 MPa	-	+	+
	All-cellulose composite Gindle 2005 (anisotropic)	-	Partially regenerated cellulose (DMAc LiCl)	13 GPa - 243 MPa	-	+	+
Compression molding	Pharmaceutical tablets	1964	Ram direction compression (cold)	10 Gpa	+	-	---
	Nilsson 2010	-	Disintegreated cellulose pulp (cold - hot pressing)	11 GPa - 76 MPa	+	-	-
	Rampinelli 2010	-	Refined micro-fibrillated cellulose (hot pressing)	180 MPa	+	-	-

*Note: in the tensile properties column, values expressed in MPa correspond to the tensile strength at break, values in GPa correspond to the modulus

III.2 Behavior of compressed cellulose under various operating condition

III.2.A Methodology and control conditions

This study basically relies on an attempt to investigate on the relationship between the molding parameters and the properties of the molded specimens. Compaction-molding parameters were defined as follow: moisture content of the α-cellulose powder introduced in the mold, quantity of powder (initial mass), pressing time, pressing temperature, molding pressure and pressurization speed (Figure III - 10). Dog-bone specimens were produced in a specially designed mold which permitted to evaluate the mechanical properties under conditions matching ISO standards for plastic materials (Chapter VI, Materials and Methods). Additionally, equilibrium moisture content and specific gravity were measured.

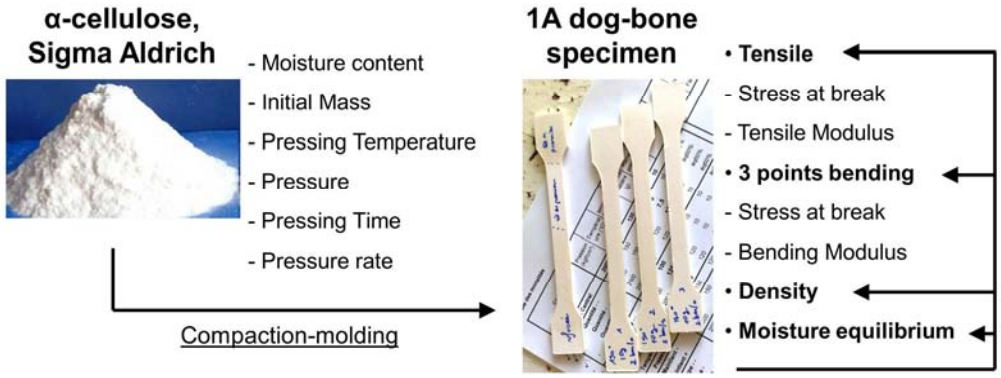


Figure III - 10: Methodology scheme for the evaluations of process's parameters effect

Control conditions of molding were chosen based on preliminary results, 60% and 25°C were common climatic conditions available in the laboratory, therefore, control moisture content for cellulose was selected as the equilibrium reached in these conditions. As the study deals with high pressure molding, control conditions have been set to the maximum pressure available in the 50 tons press (Chapter VI). 10 grams loaded in the mold, a temperature of 150°C and a time of 2 minutes were producing satisfactory results, they have been chosen as control. The pressure rate was another secondary parameter that was set to 10 bar/s as control. Table III - 2 summarizes these control conditions.

Table III - 2: Summary of control conditions for exploration study of the effect of operating conditions on the mechanical properties of compressed α-cellulose

	Pressure (MPa)	Temperature (°C)	Time (s)	Initial Mass (g)	Pressurization (bar/s)	RH (%)
Control conditions	264	150	120	10	10	60

From this starting point, parameters were changed one by one to evaluate their effect on the mechanical properties, specific gravity and equilibrium moisture content of compressed specimens. Complete results have been summarized in Table III - 3.

Table III - 3: Summary of results on compacted α-cellulose physical properties

Data / Modality		Molding parameters						Properties									
		Mass	Time	MC	Press. speed	Temperature	Pressure	Eq. MC		Specific gravity		Bending stress at break		Bending modulus		Tensile stress at break		Tensile modulus	
		g	s	%	bar/s	°C	MPa	Mean (%)	St. dev. (%)	Mean ($g.cm^{-3}$)	St. dev. ($g.cm^{-3}$)	Mean (MPa)	St. dev. (MPa)	Mean (MPa)	St. dev. (MPa)	Mean (MPa)	St. dev. (MPa)	Mean (MPa)	St. dev. (MPa)
Control		**10**	**120**	**8**	**10**	**150**	**264**	**7.02**	**0.04**	**1.503**	**0.008**	**40.2**	**3.4**	**6.18**	**0.31**	**21.2**	**1.3**	**1.60**	**0.04**
Mass	m1	**5**	control					7.02	0.07	1.502	0.008	39.7	1.7	6.50	0.24	20.7	2.1	2.61	0.22
	m2	**7.5**						6.99	0.06	1.503	0.008	38.1	2.9	6.28	0.40	21.7	1.6	1.98	0.20
	m3	**12.5**						7.11	0.04	1.503	0.008	42.4	3.0	6.78	0.32	19.3	2.1	1.37	0.05
Temperature	T4	control				**200**	control	6.86	0.16	1.513	0.008	43.2	3.4	7.17	0.35	22.4	1.5	1.73	0.11
	T3					**175**		6.87	0.02	1.510	0.003	39.9	2.4	6.19	0.18	21.1	1.0	1.59	0.05
	T2					**125**		7.22	0.02	1.505	0.004	37.3	2.7	5.62	0.23	20.0	1.2	1.55	0.09
	T1					**100**		7.56	0.06	1.490	0.007	34.7	2.9	5.39	0.22	20.1	1.8	1.55	0.05
	T0					**25**		8.57	0.03	1.481	0.002	24.5	2.4	4.43	0.43	12.0	0.5	1.27	0.04
Time	t1	control	**3**	control				7.51	0.04	1.494	0.005	35.5	1.0	6.38	0.09	18.4	0.6	1.60	0.00
	t2		**30**					7.02	0.03	1.506	0.003	39.8	1.7	5.80	0.25	20.0	1.3	1.65	0.08
	t3		**300**					6.90	0.02	1.508	0.005	36.4	2.6	5.97	0.35	20.7	1.5	1.59	0.09
Pressurization speed	R1	control			**1**	control		6.93	0.04	1.507	0.005	31.5	2.6	4.93	0.55	18.0	1.5	1.56	0.05
	R2				**2**			6.95	0.01	1.506	0.002	35.0	1.6	5.56	0.31	19.5	1.2	1.60	0.07
	R3				**50**			7.08	0.04	1.499	0.009	41.3	2.7	6.03	0.51	21.9	1.0	1.61	0.08
MC	M1	control		**0**	control			7.62	0.02	1.489	0.004	15.7	2.1	4.02	0.85	8.8	0.5	1.30	0.06
	M2			**6.1**				7.17	0.07	1.497	0.005	36.8	3.6	5.61	0.55	20.0	1.3	1.60	0.06
	M3			**10.8**				7.14	0.04	1.506	0.004	32.4	1.3	5.30	0.25	17.0	0.6	1.57	0.06
Pressure	P1	7.5	30	control	50	control	**264.3**	7.01	0.05	1.500	0.005	28.9	5.7	5.31	0.76	12.5	1.0	1.67	0.04
	P2						**132.1**	7.00	0.05	1.497	0.005	26.8	4.0	4.85	0.60	10.2	1.0	1.60	0.07
	P3						**66.1**	6.95	0.06	1.484	0.014	24.7	1.9	4.45	0.35	7.6	1.3	1.31	0.12
	P4						**44.0**	6.97	0.03	1.469	0.007	16.7	3.9	3.29	0.58	6.5	1.0	1.29	0.04
	P5						**30.8**	6.95	0.05	1.459	0.009	14.0	2.6	2.88	0.36	4.7	1.0	1.17	0.10
	P6						**17.6**	7.11	0.04	1.425	0.011	6.2	1.4	1.49	0.21	3.3	0.3	0.92	0.09
	P7						**8.8**	7.07	0.07	1.392	0.007	3.0	0.3	0.74	0.08	1.0	0.1	0.57	0.03

III.2.B Effect of mass loaded in the mold

Control conditions (10 g of cellulose loaded in the mold) produced specimens with a thickness of 3.61 ± 0.10 mm. 12.5, 7.5 and 5 grams were tested in order to evaluate changes on the molded specimens. Lower mass than 5 g could not be tested because low quantity of material could not be filled homogeneously in the mold which conducted to white spots, locally weaker materials, high scattering thus unreliable data. First of all, thickness was measured and mean and standard deviations calculated on 14 specimens (Table III - 4).

Table III - 4: Thickness-mass relationship upon mass variation

Mass	Thickness	
	Mean	St dev.
5	1.9	0.10
7.5	2.8	0.10
10	3.6	0.13
12.5	4.5	0.14

The change of mass loaded in the mold followed a linear law with a non-null constant coefficient (Figure III - 11). There is a certain deviation from the expected origin (zero) which would indicate that materials produced from a higher mass would have a lower thickness than expected. Probably, the better homogeneity while filling the mold with larger quantity of cellulose explains this.

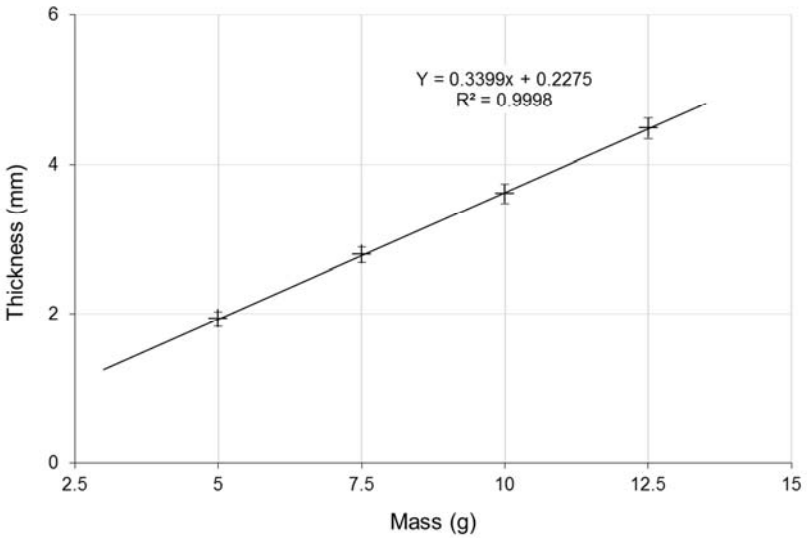


Figure III - 11: Thickness-mass relationship and linear regression upon mass change

Secondly, mechanical properties tests indicated that all parameters were kept approximately constant upon variation of mass except for the tensile modulus which was drastically increased with the decrease of mass loaded in the mold (Figure III - 12).

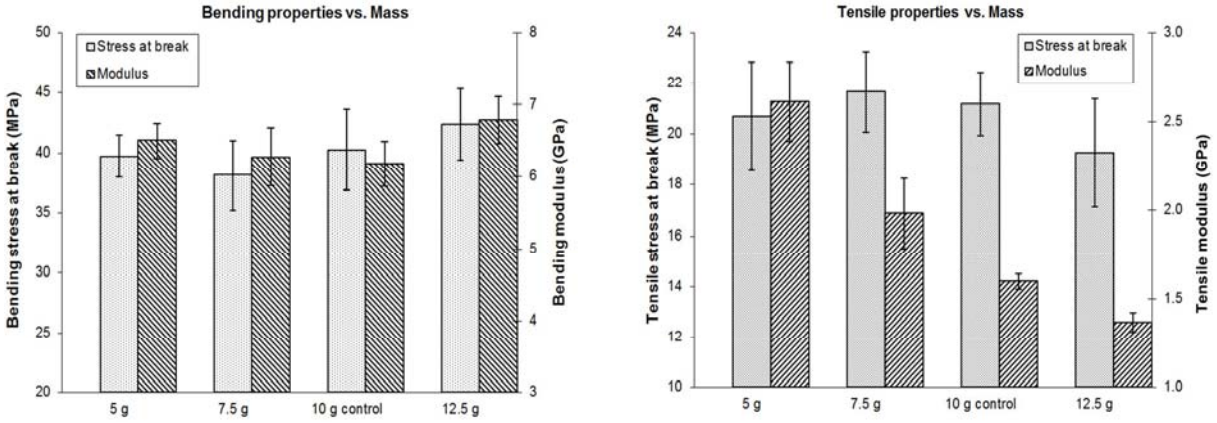


Figure III - 12: Effect of mass on the mechanical properties of compressed α-cellulose samples

Bending properties are much affected by the surfaces of the specimen, because during the bending, the upper surface is compressed and lower surface stretched. With a drastic increase of the tensile modulus it was concluded that certain heterogeneity existed within the material: as the molding conditions were identical, the surfaces (later called skin) must have been kept the same. Increasing thickness, let to specimens with identical skin thickness but a thicker core which decreased the skin / core ratio. The surface of the material expressed a higher modulus than the core, but a comparable strength. This characteristic of brittle materials accommodates very well with optical observations made on the surface that appears true, shiny and plastic-like. As for the specific gravity, it wasn't measured to be different between the core and the skin and so was equilibrium moisture content (Table III - 3). For later experiments, because of these results obtained on the effect of mass loaded in the mold, 7.5 g will be selected as a new reference for saving material consumption when preparing specimens.

III.2.C Effect of processing time

Classical molding time of 10 and 20 minutes are found in the literature in binderless boards pressing, very few data are available on high pressure molding (6 minutes has been mentioned by Rampinelli et al. 2010) yet, preliminary results showed that shorter times produced satisfactory results. From the control 2 minutes, 3 and 30 seconds were tested as trials of shortened operating time, 5 minutes was chosen to evaluate the effect of increased molding time.

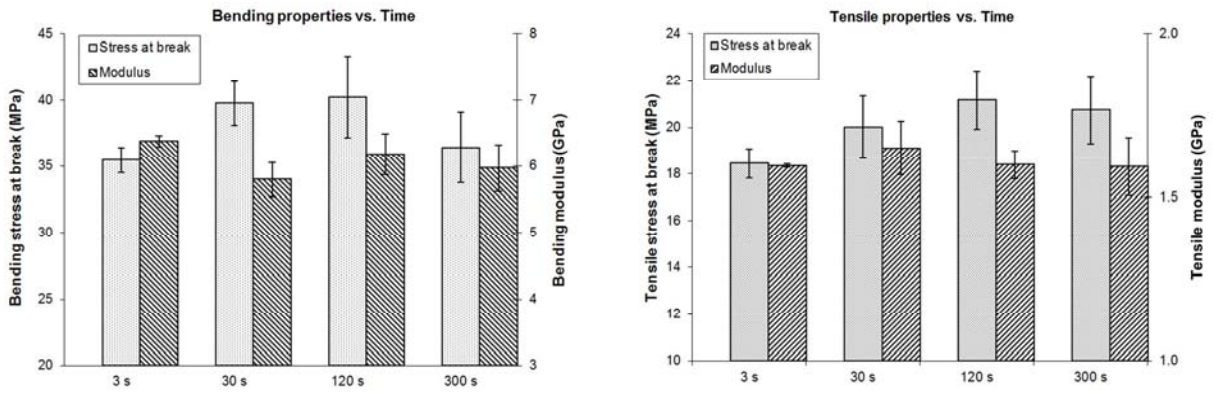


Figure III - 13: Effect of time on the mechanical properties of compressed α-cellulose samples

Surprisingly, time did not produce much effect (Figure III - 13). Statistical tests were performed and the difference were concluded to be non-significant according to Scheffé test, data available in the first published paper (Pintiaux et al. 2013). The independence of the mechanical properties and molding time was an encouraging result, showing that low times of molding could be operated which would save time, energy and facilitate industrialization. The average strengths of 3 seconds however appeared slightly lower than the others (Table III - 3), these specimens also had a slightly higher equilibrium moisture content (MC) and lower specific gravity (SG) which would indicate a lower cohesion. Therefore, for later experiments, and also for saving time on the experiments 30 seconds have been considered as reference.

III.2.D Effect of cellulose moisture content

From the control MC of 8% (equilibrium 60% RH 25°C), variations were investigated, α-cellulose was dried in an oven at 103°C at least for 48 hours to produce dry α-cellulose. Climatic chambers at 45% RH 25°C and 75% RH 25°C respectively produced α-cellulose at 6.1 and 10.8 % MC (Table III - 5).

Table III - 5: Moisture content conditions for the evaluation of the effect of moisture content on the mechanical properties of compressed α-cellulose samples

Temperature (°C)	Relative Humidity (%)	Measured Moisture Content (%)
103	0	0
25	45	6.1 ± 0.1
25	60	8.0 ± 0.0
25	75	10.8 ± 0.1

Drastically lower mechanical properties, higher specific gravity, and higher equilibrium moisture content were observed on specimens molded from dry powder. A lighter color and a rougher surface aspect were observed. Equilibrium MC of these specimens was also higher and SG lower suggesting self-bonding to a lower extent (Table III - 3). Moisture was thus concluded to be necessary to achieve satisfactory molding in these conditions. This apart, not much effect could be observed upon moisture content variation in the range 6 – 11% (Figure III - 14). High moisture produced slightly lower strengths.

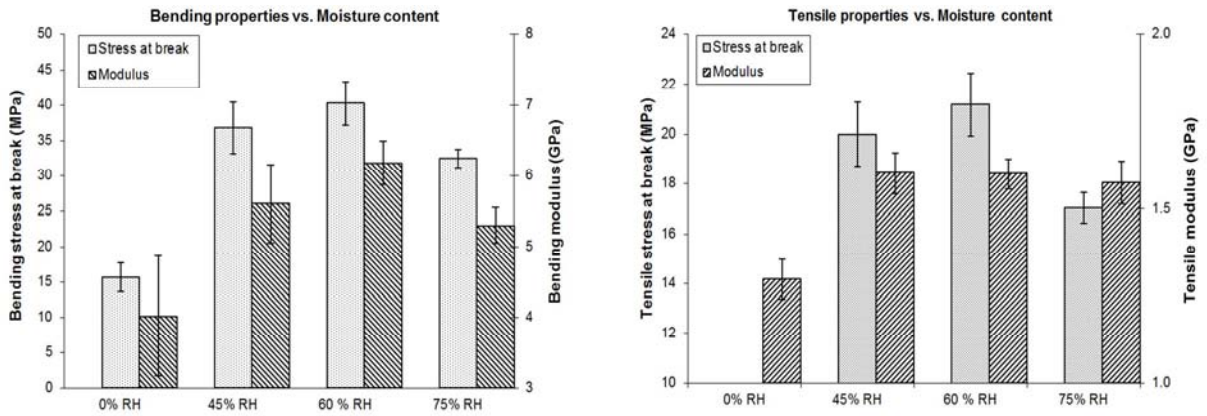


Figure III - 14: Effect of moisture content on the mechanical properties of compressed α-cellulose samples

Because highest mechanical properties were obtained on control conditions of molding, this condition was kept as a reference. The effect of moisture, however remained of primary interest, as the removal of water from the powder produced drastically different results. Moisture content remained one of the primary parameter to study, and was later further investigated.

III.2.E Effect of pressurization speed

Parallel could be made between this work and the production of pharmaceutical tablets. In this industry, α-cellulose can be used as excipient, i.e. as an inert substance for the active drugs to be dispersed in and that can form the tablet for ingestion. Even though compaction speed are much higher than those that can be applied in the laboratory press (Akande et al. 1997), its effect was investigated. Of course, in this experiment, a choice had to be made because pressurization speed, time and pressure are not independent. The integral time.pressure was chosen to be maintained constant, thus when pressurization rate was decreased total molding time increased to maintain an equal time.pressure integral. Explanations can be found in the materials and methods part (Chapter VI).

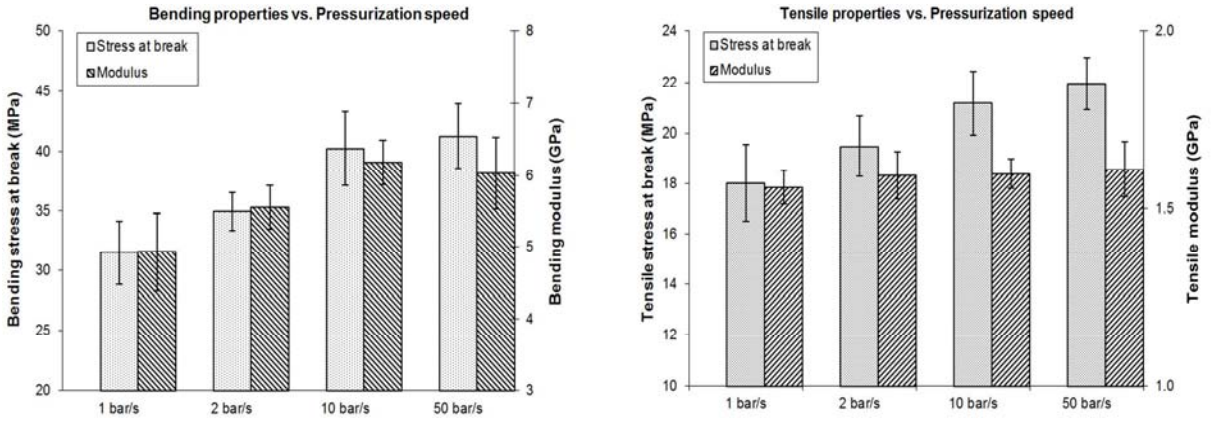


Figure III - 15: Effect of pressurization speed on the mechanical properties of compressed α-cellulose samples

The properties were seen to be slightly degraded when decreasing pressurization speed (Figure III - 15) which could also be an effect of higher time due to thermal degradation (Figure III - 13), lower pressure, or a combination of both. Anyway, higher pressurization speed produced specimens with slightly higher mechanical properties. Also, increasing pressurization speed allowed to slightly lower operating time. 3D molding also had benefits from increasing pressurization speed. Thus, next experiments would have preferentially highest pressurization speeds as a new reference.

III.2.F Effect of temperature

During the first set of experiments, the mechanical properties increased linearly with processing temperature (Figure III - 16). In the same time, specific gravity was increased and equilibrium moisture content was decreased, showing reorganization and less availability on the hydroxyl groups. At 200°C, about 1/3 of the specimens were delaminated (thus discarded from the results), thus more specimens were produced to calculate mean and standard deviation. 200°C appeared to be a limit, which was a classical result in the literature (Chapter I).

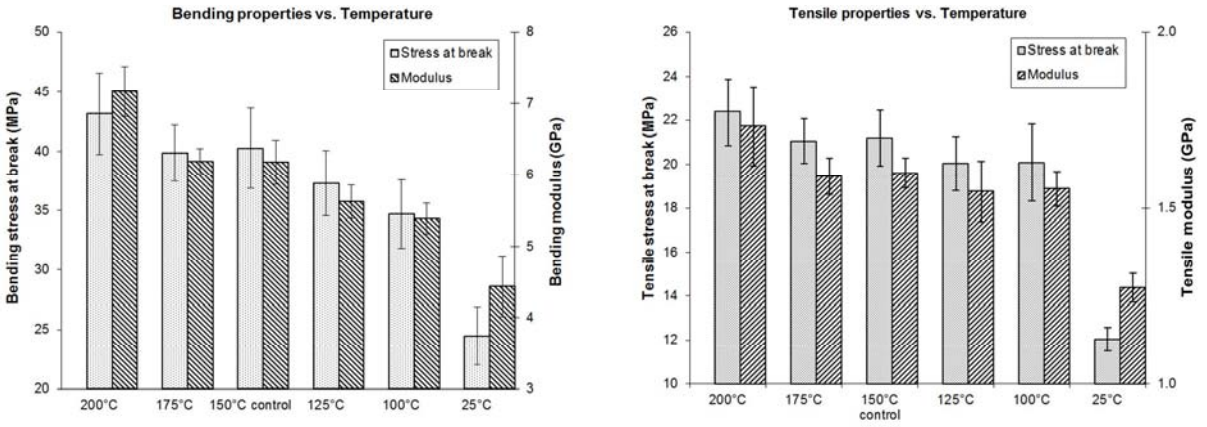


Figure III - 16: Effect of temperature on the mechanical properties of compressed α-cellulose samples

Yet, the understanding of this phenomenon was limited because delamination occurred only "sometimes". One possible explanation would be the time needed to load the powder in the hot mold, a slightly longer time to load the mold would lead to a much higher moisture loss from the powder. More experiments were later performed to understand the moisture / temperature effect on delamination (see III.3).

As can be observed on the SEM pictures taken in Nagoya (Figure III - 17), the inter-particle voids are decreasing from 30 to 200°C, showing a higher deformability of the particles with increased temperatures, which explains the increased density and could be an explanation for the better mechanical properties observed upon increasing molding temperature (Table III - 3).

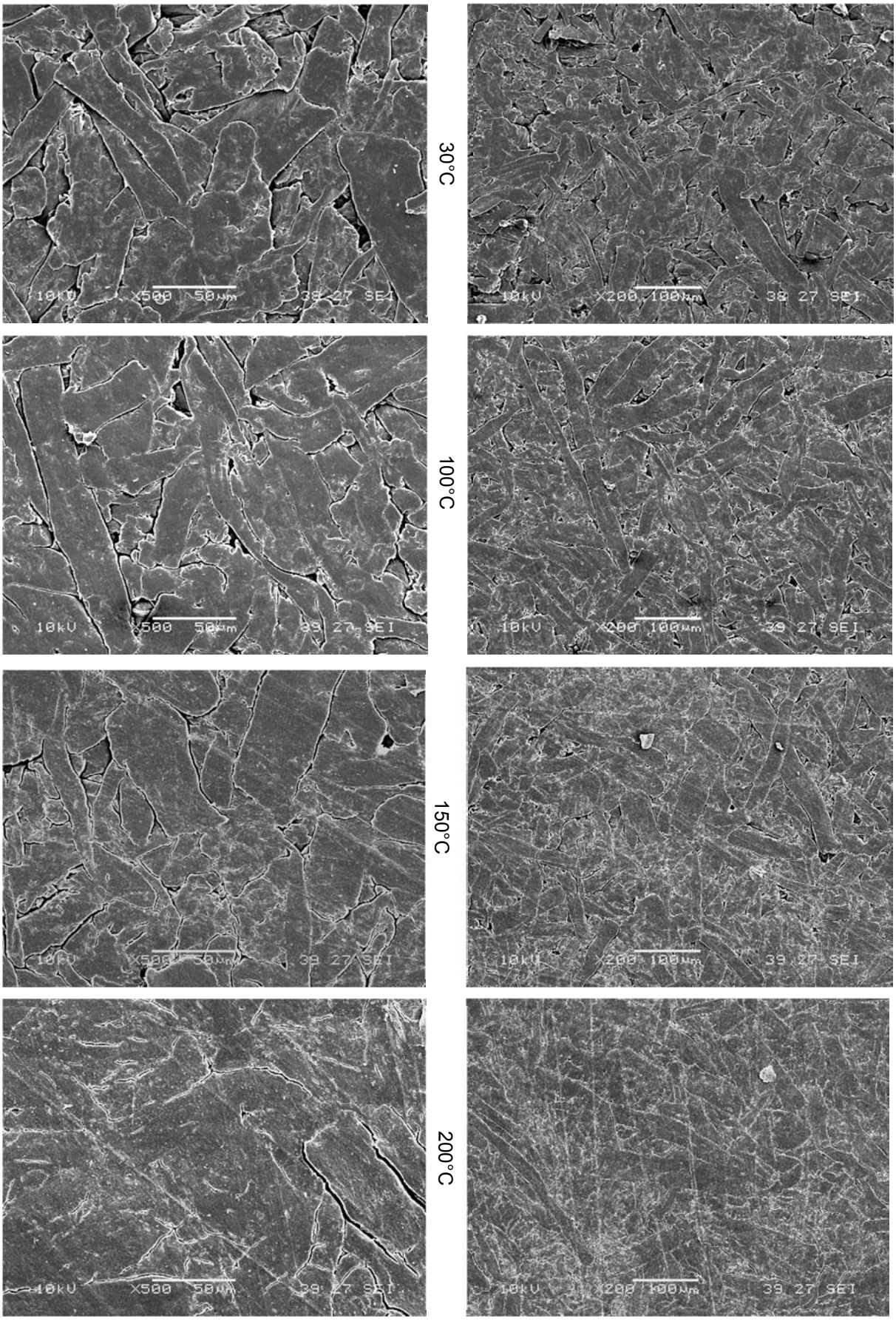


Figure III - 17: SEM pictures of specimens' surface produced at different temperatures

III.2.G Effect of pressure

In the industrial processing of wood-based panels, cellulose is considered a passive polymer, i.e. does not participate actively to the cohesion although lignin and hemicelluloses do. Products of degradation, however could participate to cohesion through the hydroxymethylfurfural route (Chapter I). Anyway, without pressure, no cohesion was expected on pure cellulose, and as this work deals with high pressure molding, low pressure molding was not considered in the first times. A first conclusion was that no significant difference could be observed between specimens compacted at 133 or 265 MPa (Pintiaux et al. 2013). Later, complementary experiments were performed: new control conditions were a pressing temperature of 150°C (average), 8% (control moisture content), 30 seconds (low molding time), 50 bar/s (highest pressurization speed), 7.5 g (reduced mass) and pressure was varied from 8.8 to 264 MPa (Table III - 3).

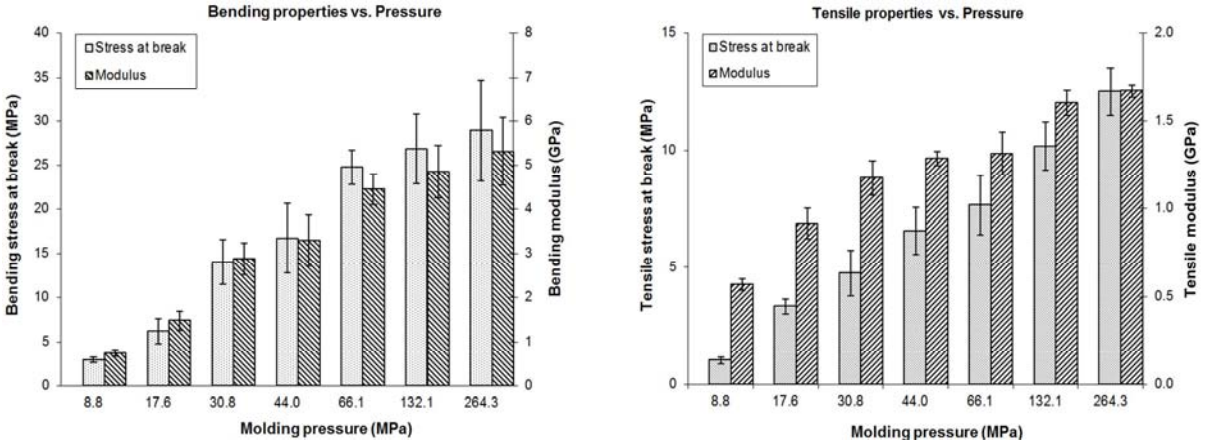


Figure III - 18: Effect of pressure on the mechanical properties of compressed α-cellulose samples

As expected, the mechanical properties increased with pressure (Figure III - 18). The increase rate of the mechanical properties is decreasing with pressure which means that the effect of pressure was less and less important, therefore, it is possible to consider that sufficient properties could be obtained (depending on the requirements) with much lower pressure than 264 MPa. In the meantime, specific gravity was increased and thickness decreased, the specific mechanical properties (i.e. mechanical properties divided by the specific gravity of specimens) were then calculated (Table III - 6) and drawn in (Figure III - 19).

Table III - 6: Specific and standard mechanical properties of compressed α-cellulose samples under various conditions of pressure

Hydraulic pressure	Molding pressure	Thickness		Specific gravity		Bending stress at break			Bending modulus			Tensile stress at break			Tensile modulus		
						Specific	Standard		Specific	Standard		Specific	Standard		Specific	Standard	
		Mean	St. dev.	Mean	St. dev.	Mean	Mean	St. dev.	Mean	Mean	St. dev.	Mean	Mean	St. dev.	Mean	Mean	St. dev.
bar	MPa	mm		g/cm³		MPa.cm³/g	MPa		GPa.cm³/g	GPa		MPa.cm³/g	MPa		GPa.cm³/g	GPa	
300	264.3	2.60	0.04	1.500	0.005	19.3	28.9	5.7	3.5	5.31	0.76	8.3	12.5	1.0	1.1	1.67	0.04
150	132.1	2.75	0.05	1.497	0.005	17.9	26.8	4.0	3.2	4.85	0.60	6.8	10.2	1.0	1.1	1.60	0.07
75	66.1	2.90	0.06	1.484	0.014	16.7	24.7	1.9	3.0	4.45	0.35	5.2	7.6	1.3	0.9	1.31	0.12
50	44.0	3.03	0.05	1.469	0.007	11.4	16.7	3.9	2.2	3.29	0.58	4.5	6.5	1.0	0.9	1.29	0.04
35	30.8	3.13	0.06	1.459	0.009	9.6	14.0	2.6	2.0	2.88	0.36	3.3	4.7	1.0	0.8	1.17	0.10
20	17.6	3.46	0.04	1.425	0.011	4.4	6.2	1.4	1.0	1.49	0.21	2.3	3.3	0.3	0.6	0.92	0.09
10	8.8	4.14	0.07	1.392	0.007	2.1	3.0	0.3	0.5	0.74	0.08	0.7	1.0	0.1	0.4	0.57	0.03

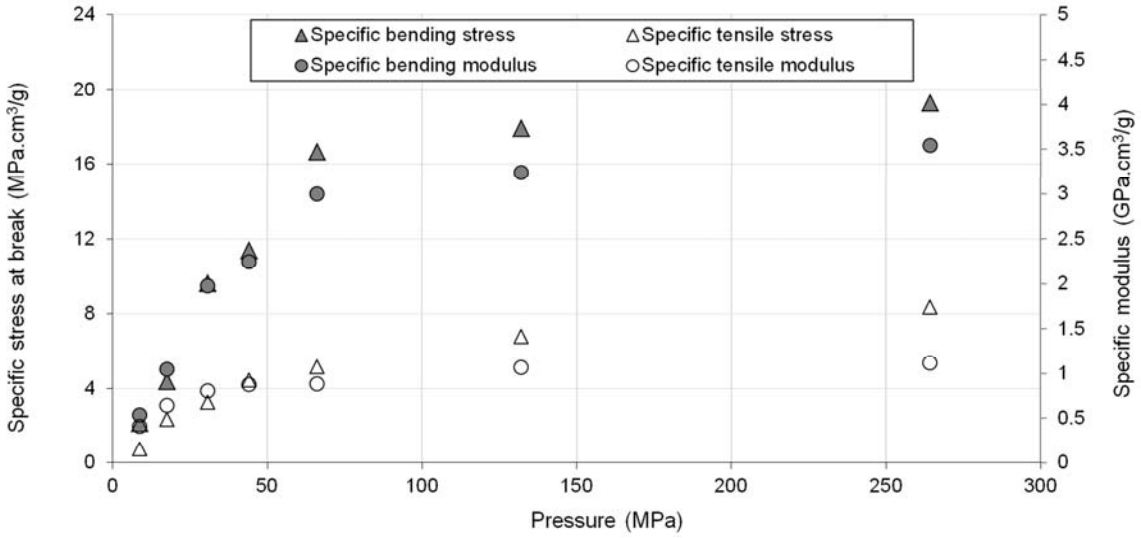


Figure III - 19: Effect of pressure on the specific mechanical properties

The specific mechanical properties were seen to increase following a logarithmic law which would show that not only densification governs the mechanical properties, but also some cohesion mechanism that does not involve densification (but reorganization) could occur.

III.3 The cliff behind the hill: investigating the interdependency of temperature and moisture content on the mechanical properties and delamination

III.3.A Delamination mapping

The temperature of molding is generally reported to be the most important parameter of improvement for the properties of binderless boards. Delamination is often reported as a physical limit to the increase of temperature way before thermal decomposition (as it could be expected). It is also reported as a technological limit in the pharmaceutical tablets production. Delamination also causes troubles in the industry of wood-based panels with adhesives (Chapter I): moisture is needed because it facilitates the heat transfer from the heated press plates through the surfaces of the mat to the inner layers of the pressed material in order to cure the resin. Yet, an excess of moisture is known to let steam accumulate in the inner layers and trigger delamination. Also because free water reacts with the resin, moisture content is commonly reduced to about 3% prior to molding.

Surprisingly, reduced moisture content has been rarely reported in the experiments about binderless boards pressing although results were very encouraging (Nonaka et al. 2013). First results obtained during the present work concluded that moisture content had a limited impact on the mechanical properties in control conditions as defined in Table 2. At 8% MC and 200°C, delamination was observed for about 1/3 of the molded specimens. Only the 2/3 left was tested and exhibited the best mechanical results so far. There is thus a discontinuous behavior of the effect of temperature on the mechanical properties: there is a regular increase of the properties upon increase of temperature until a certain temperature that triggers delamination. Moisture reduction was expected to allow an increase of the molding temperature, but the effect of the moisture decrease / temperature increase on the mechanical properties has to be evaluated.

Thus, in a second time, the effect of moisture and temperature were deeper investigated, high temperature range from 175°C to 250°C (laboratory press maximum temperature) and low moisture range (0 to 8%) were selected. 14 dog-bone specimens were compression-molded for each of the 20 conditions (175 – 200 – 225 – 250°C crossed with 0 – 2 – 4 – 6 – 8 % MC). For these experiments, the control conditions were 7.5g of α-cellulose introduced in the mold, a molding time of 30 seconds and a pressure rate increase of 50 bar/s. Results on delamination, based on the simple observation of the specimens were sum up in Table III - 7.

Table III - 7: Molding results on the moisture / temperature experiments

Moisture content	Temperature 175°C	200°C	225°C	250°C
8	ok	delaminated	slightly delaminated	ok
6	ok	slightly delaminated	ok	ok
4	ok	ok	ok	ok
2	ok	ok	ok	ok
0	ok	ok	ok	ok

At 175°C, no delamination was observed whatever the moisture content. At 8%, delamination was confirmed for 200°C, about half of the specimens were separated in two, the other half seemed to remain sound but a crack actually existed along the edge of the dog-bone (Figure III - 20). These specimens were not mechanically tested.

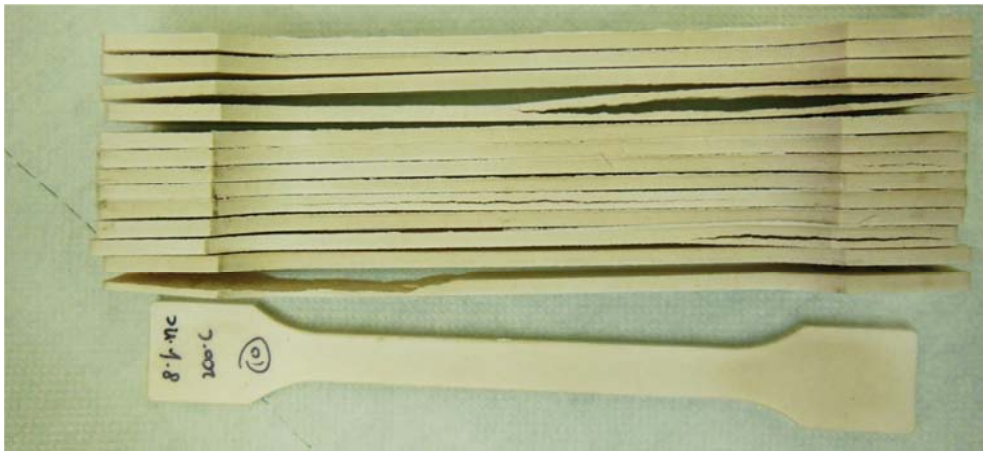


Figure III - 20: compressed α-cellulose samples at 200°C and 8% showing important delamination

Surprisingly, increasing the temperature decreased the effect of delamination and only some of the specimens exhibited slight cracks at 225°C, none of the specimens were truly delaminated and, at 250°C all the specimens were perfectly sound. At 0, 2 and 4 %, none of the temperatures were causing troubles of delamination. Finally, for 6% of moisture content, 200°C of molding temperature made slight cracks appear on the edge of some specimens but later on, at 225 and 250°C the specimens showed no defects.

This mapping of the conditions that triggers delamination was thus successfully obtained. It was confirmed that 200°C and 8% MC were the worst conditions of molding because heavy delamination occurred. Increasing temperature made the delamination phenomena decrease at 225°C and disappear at 250°C. Decreasing moisture to 6% decreased the delamination phenomenon, and a further decrease of the MC to 4 – 2 and 0 % made it disappear. It was concluded that delamination could be avoided if the conditions were kept far from the 200°C – 8% point.

III.3.B Color scale

As can be seen on Figure III - 21, the color of the compressed specimens is gradually darkening with the temperature which is really obvious, but within a temperature, the moisture content had much less effect; there might be a slight correlation between lower moisture and darker color. The 2% series might also appear slightly less dark than the others, they also presented the highest mechanical properties. The color of the specimens seems to be influenced by their density (and possibly heterogeneity) and the temperature of molding. The link between color of the specimens and the mechanical properties was not further studied, but it may be valuable in the future.

III.3.C Mechanical properties mapping

Except for the 200°C – 8% specimens, the 15 remaining conditions were tested in tensile and bending tests. The results are gathered in Table III - 8. It can be observed that the specimens processed at 2% moisture content, whatever the temperature had much higher mechanical properties than the others.

Table III - 8: Summary of the mechanical properties of moisture content / temperature effect experiment, the 2 % experiments appear in bold letters

		Temperature								
		175°C		200°C		225°C		250°C		
		Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	
Moisture content (%)	8	34.75	3.92	ND		30.24	5.38	37.02	2.04	Bending strength (MPa)
	6	35.65	2.64	39.93	4.27	40.23	2.96	44.485	1.46	
	4	35.21	2.59	34.92	5.02	41.73	1.79	44.84	3.15	
	2	**43.17**	**6.29**	**45.30**	**7.78**	**55.09**	**4.70**	**70.10**	**4.14**	
	0	35.00	1.79	41.13	2.03	39.62	3.38	51.73	5.74	
	8	5.94	0.59	ND		6.23	0.44	7.11	0.33	Bending modulus (GPa)
	6	5.62	0.30	6.16	0.58	6.30	0.40	7.04	0.45	
	4	6.13	0.38	6.03	0.66	6.94	0.24	7.40	0.46	
	2	**6.10**	**0.44**	**6.20**	**0.70**	**7.24**	**0.34**	**8.09**	**0.67**	
	0	5.67	0.32	0.04	0.63	6.71	0.33	7.72	0.26	
	8	17.19	1.24	ND		16.17	3.03	19.16	1.00	Tensile strength (MPa)
	6	22.30	1.85	15.29	8.77	25.09	3.20	27.55	1.92	
	4	18.39	2.47	20.37	1.87	20.59	1.55	22.80	3.93	
	2	**19.15**	**1.70**	**23.35**	**1.45**	**24.27**	**3.13**	**31.13**	**5.91**	
	0	18.14	1.28	16.45	3.42	20.62	1.11	25.22	1.33	
	8	1.88	0.10	ND		1.96	0.03	1.99	0.07	Tensile modulus (GPa)
	6	1.91	0.11	1.75	0.06	2.03	0.14	2.02	0.11	
	4	1.99	0.04	2.00	0.07	2.05	0.11	2.13	0.11	
	2	**1.78**	**0.08**	**1.84**	**0.05**	**1.87**	**0.08**	**1.94**	**0.15**	
	0	1.83	0.10	1.82	0.07	1.94	0.09	2.00	0.08	
		Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	
		175°C		200°C		225°C		250°C		

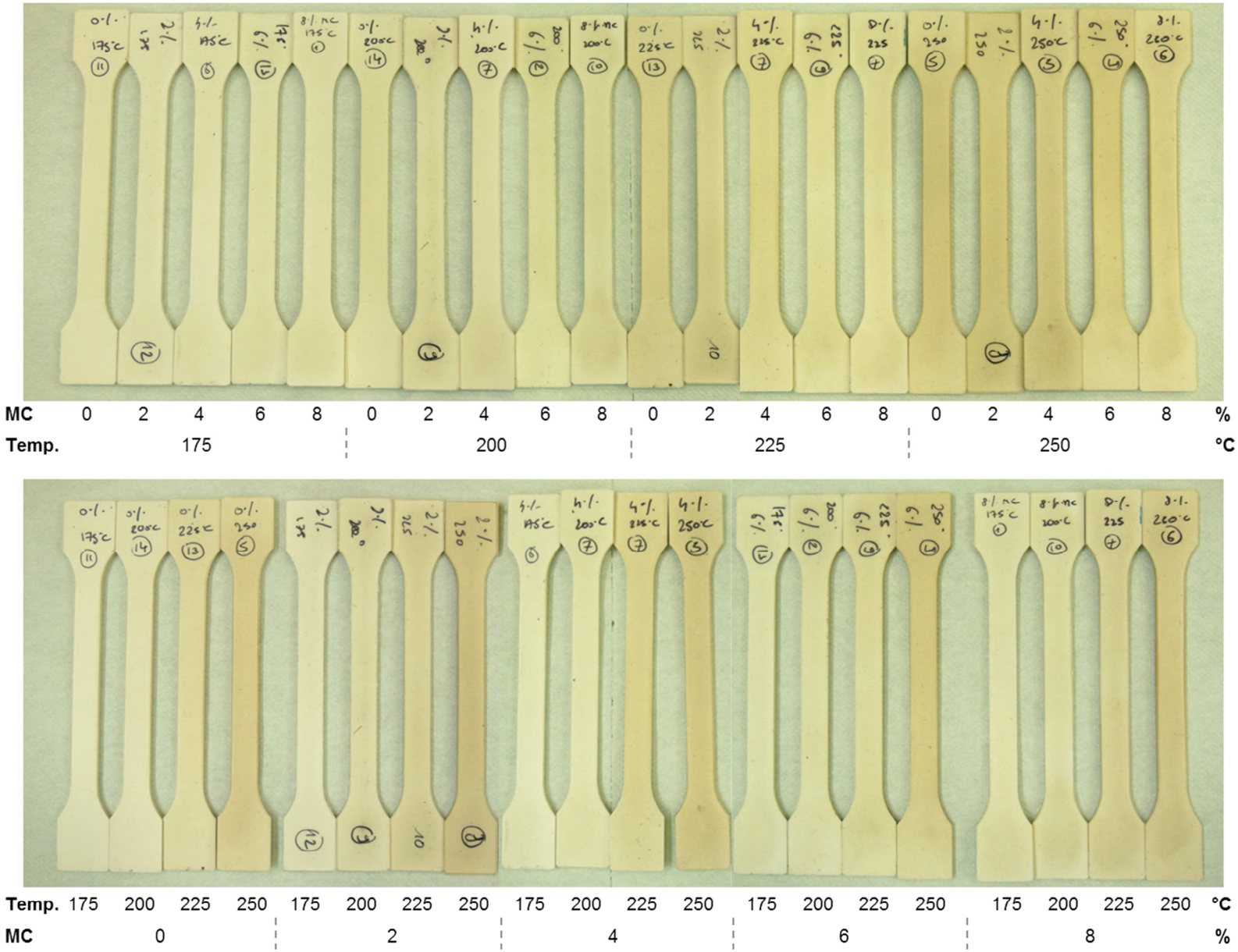


Figure III - 21: Pictures of moisture/temperature mapping samples and differences of colour sorted by moisture – temperature (first picture) and temperature – moisture (second picture)

The mechanical properties of 8%-225°C samples were the lowest within the whole set of conditions, which is a direct effect of the slight delamination experienced during these conditions. The 6%-200°C which also produced a slight delamination had the lowest tensile strength but the bending strength was in the average. Except for these two points, increasing temperature at constant MC generally led to an increase of the mechanical properties. The tensile modulus shows very little variation within the experiments range.

Table III - 9: Bending strength (MPa) on the left and Tensile strength (MPa) on the right, mean values for the MC / Temperature with a colour scale blue – red

Moisture content (%)	Temperature 175°C	200°C	225°C	250°C
8	34.75	ND	30.24	37.02
6	35.65	39.93	40.23	44.5
4	35.21	34.92	41.73	44.84
2	43.17	45.30	55.09	70.10
0	35.00	41.13	39.62	51.73

Moisture content (%)	Temperature 175°C	200°C	225°C	250°C
8	17.19	ND	16.17	19.16
6	22.30	15.29	25.09	27.55
4	18.39	20.37	20.59	22.80
2	19.15	23.35	24.27	31.13
0	18.14	16.45	20.62	25.22

Table III - 10: Bending Modulus (GPa) on the left and Tensile modulus (GPa) on the right, mean values for the MC / Temperature with a colour scale blue – red

Moisture content (%)	Temperature 175°C	200°C	225°C	250°C
8	5.94	ND	6.23	7.11
6	5.62	6.16	6.30	7.04
4	6.13	6.03	6.94	7.40
2	6.10	6.20	7.24	8.09
0	5.67	6.37	6.71	7.72

Moisture content (%)	Temperature 175°C	200°C	225°C	250°C
8	1.88	ND	1.96	1.99
6	1.91	1.75	2.03	2.02
4	1.99	2.00	2.05	2.13
2	1.78	1.84	1.87	1.94
0	1.83	1.82	1.94	2.00

At 175°C, except for the 2% MC, the mechanical properties were about the same all within the moisture range. At 200 and 225°C, the behavior of moisture is quite difficult to analyze especially for the stresses. The bending modulus has a quite smooth response (Table III - 10) the highest value is for 2% - 250°C and lowering temperature or increasing / decreasing moisture lead to a gradual decrease of the bending modulus. The tensile modulus showed a lower response to the variations of temperature than the other parameters.

Specimens produced at 2% - 250°C had remarkable properties and were the best specimens ever produced during this research work. The difference between 2 % and the other values of moisture was so drastic that the experiments were doubled as verification. However, compared to the other solid materials (Table III - 1), the mechanical properties obtained are quite low, and comparable to paper.

The slope of increase of the mechanical properties is high from 200 to 250°C, and the properties of specimens obtained at higher temperature is a burning question ! Unfortunately these experiments could not be performed because 250°C was the temperature limit on the laboratory press. Cellulose starts to degrade around 220-230°C, but the effect of degradation on the mechanical properties is uncertain (Figure III - 7). A lower DP would probably affect negatively the strengths, but the "sugar" chemistry could have a bonding effect through the hydroxymethyl furfural route (see Chapter I).

III.4 Correlation of equilibrium moisture content and density of the compressed specimens

From the first set of experiments (Pintiaux et al. 2013), the equilibrium moisture content and specific gravity of the compressed specimens were plotted and it was observed that within this first set of data the equilibrium moisture content was quite correlated to density (Figure III - 22).

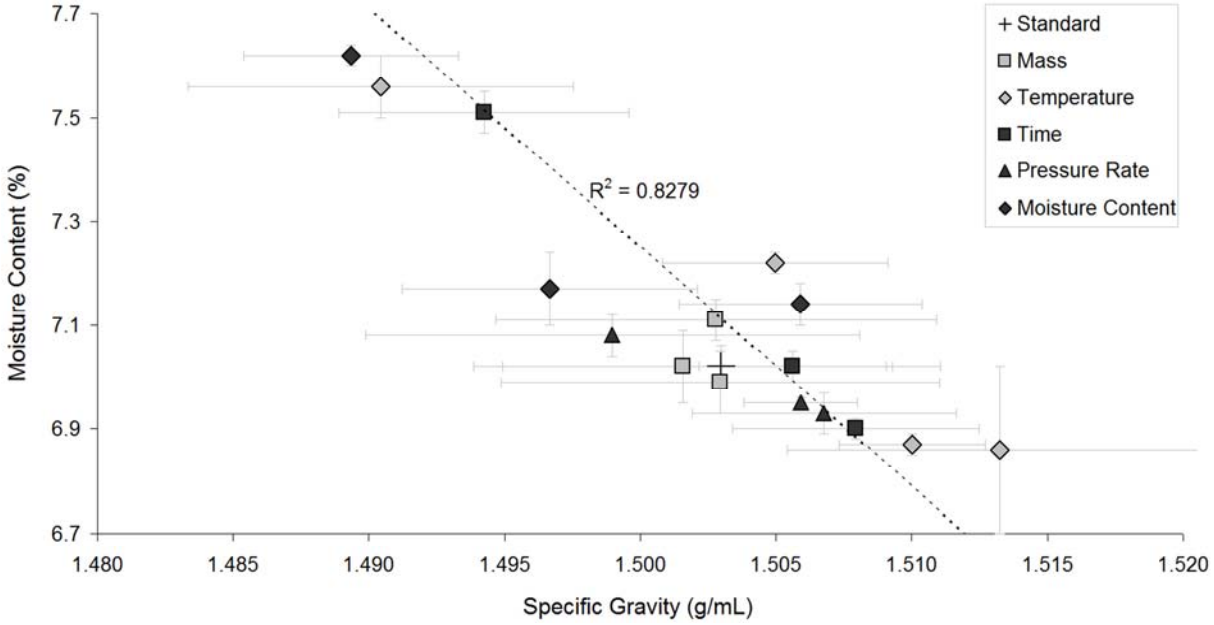


Figure III - 22: MC correlated to specific gravity (first set of experiments, evaluation of different parameters)

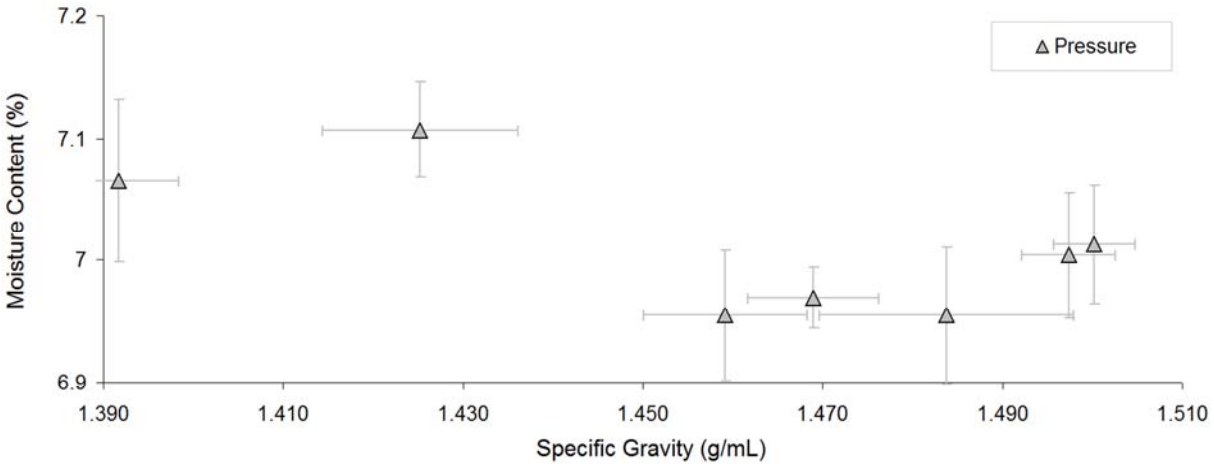


Figure III - 23: MC correlated to specific gravity (second set of experiments, evaluation of pressure)

The reliability of the data being what it is (high standard deviation of the specific gravity measurements) the later interpretation has to be considered with care: Most of the parameters tested in the published paper except mass (i.e. III.2.A to III.2.F), contributed to

draw a correlation between MC and density. In other terms, in this first set of experiment, the loss of accessibility of free hydroxyl groups appeared correlated to the loss of porosity, i.e. increased density (Figure III - 22). But in the "molding pressure" set of experiment (Figure III - 23), when the pressure was evaluated alone (and control conditions slightly changed i.e. mass changed from 10 to 7.5g, time from 2 minutes to 30 seconds, pressure rate from 10 to 50 bar/s, temperature from 150 to 175°C) there was no correlation between MC and density.

This would show that all parameters except pressure induced changes in the compressed specimens what were observable on changes of density and MC in a correlated way that suggest a loss of accessibility of the free hydroxyl groups; possibly due to a higher level of organization (higher crystallinity) thus the hypothesis can be made that pressure only acts as a catalyst when the other parameters (temperature, time and moisture) triggers changes in MC and density. This hypothesis could be verified by producing specimens while varying pressure, temperature, time and moisture simultaneously for instance using an efficient experimental design.

III.5 Humid atmosphere, water and time properties of compaction molded α-cellulose specimens

III.5.A Humid atmosphere behavior

28 control specimens (175°C – 7.5g – 30 s – 264 MPa – 50 bar/s) - that were equilibrated for about 1 month - were separated in 2 lots, the first was pre-weighted, their thickness measured and taken for 15 days in a climatic box at 85% RH and 25°C while the others stayed at 60%RH. The samples were all re-weighted and measured prior to being tested in bending.

The water uptake, from 60 to 85 % RH at 25°C (15 days) was measured to be 2.35 ± 0.04 %. In the same time, the thickness of the specimens was increased by 6.2 % which confirms the poor stability of the compressed cellulose specimens under moist atmosphere at control conditions of molding. The mechanical properties were significantly reduced as seen on Table III - 11. It was also noticed that the specimens had mechanical properties lower than the usual controls. Probably because of the time taken between the molding time and testing time after what it was decided to measure the aging of the specimens (see below, Time stability experiment).

Table III - 11: Mechanical properties of specimens submitted to 15 days under 85% RH 25°C atmosphere

	Thickness (mm)		Bending stress at break (MPa)		Bending modulus (GPa)		Tensile strength at break (MPa)		Tensile modulus (GPa)	
	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.	Mean	St. dev.
Control	2.73	0.10	35.9	3.6	5.25	0.41	15.5	2.2	1.45	0.12
85% RH	2.90	0.10	22.0	1.1	3.14	0.29	10.3	0.8	1.35	0.02

III.5.B Water resistance measurements

The water resistances were measured on 2 different molding conditions in order to serve as comparison for later work extended to lignocellulosic materials. The water absorption (WA) and thickness swelling (TS) of control conditions i.e. 175°C – 8% MC and 250°C – oven-dried 0% MC were evaluated.

Results are available in Table III - 12. High water sensitivity was expected from the cellulose samples, but the values collected during the WA/TS tests were surprising:

Table III - 12: Water absorption and thickness swelling of compressed cellulose samples

175°C - 8%				250°C - 0%			
WA		TS		WA		TS	
mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.
75%	2%	96%	3%	65%	4%	79%	2%

The water properties of the cellulose specimens was later seen to be better than any other plan materials tested in the same conditions (Chapter V). An interesting fact is that they were all cracked from the middle, precisely where, if delamination had occurred, the specimen would have been opened (Figure III - 24)

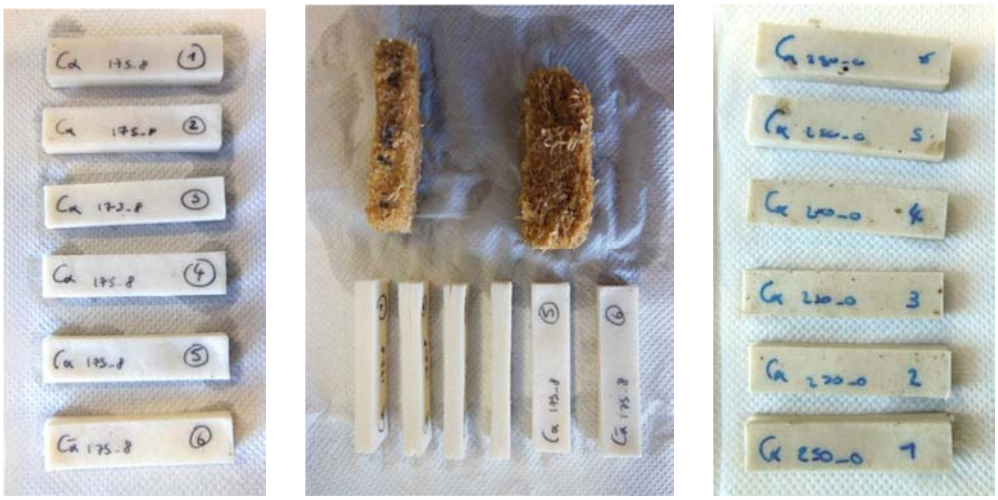


Figure III - 24: Cellulose water properties specimens, from the left to the right: 175°C-8% specimens, compared to WS1 specimens, 250 – 0% specimens.

III.6 Time stability of compressed specimens

In the early stages of this work, the mass of the specimens was observed to be constant after about 4 days to 1 week. Later an experiment was performed in order to evaluate the evolution of the mechanical properties during the equilibrium time and after. 35 specimens of the control conditions (175°C – 7.5g – 30 s – 264 MPa – 50 bar/s) were produced in a row, weighted and their thickness measured precisely 1 minute and again 1 hour after their molding

Between the moment of demolding (1 minute after demolding) and 1 hour under room conditions (20°C ~50% RH) the weight of the 16 first specimens increased by 0.52 ± 0.16 % while the thickness was increased by 0.84 ± 0.85% (i.e. a mean mass gain of 0.037 ± 0.011 g per specimen). The variation of thickness were not reliable because of the precision of the digital caliper used (0.01 mm) but the mass increase during this first hour was significant and about twice higher than the change of mass that occurred during the next 2 months of kinetic measurements.

Table III - 13: Aging tests results

Days	Δ mass		Δ thickness		Bending strength (MPa)		Bending modulus (GPa)	
	mean	st. dev.	mean	st. dev.	mean	st. dev.	mean	st. dev.
0	0		0		51.4	3.0	6.34	0.03
2	0.14	0.02	0.01	0.02	50.8	2.3	6.67	0.03
4	0.19	0.02	0.05	0.09	45.0	4.9	6.47	0.04
8	0.21	0.02	0.08	0.04	42.9	3.5	5.90	0.02
15	0.20	0.01	0.06	0.03	43.3	4.5	6.31	0.05
30	0.22	0.01	0.10	0.04	43.1	2.3	6.70	0.03
60	0.20	0.10	0.11	0.08	44.4	2.1	6.40	0.02

This 1 hour measurement was used to set the initial time of the aging experiment. The first 5 specimens were tested in bending right away. Then, 5 specimens were weighted and tested again after equilibrium of 2, 4, 8, 15, 30 and 60 days. The results were gathered in Table III - 13. It was noticed a negative correlation between the mass gain and the bending strength (Figure III - 25). The modulus showed less variation and no correlation.

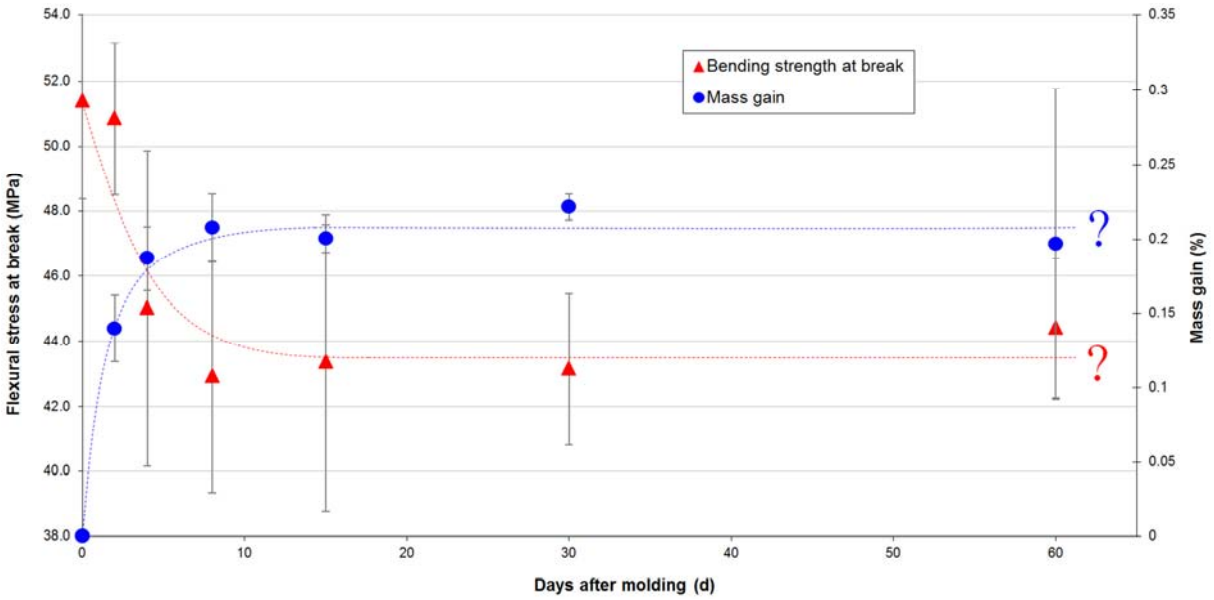


Figure III - 25: Bending strength at break correlated to the weight variation of control specimens, standard deviation calculated from 5 repetitions

This experiment did not permitted to detect an ageing of the specimens although specimens tested at different times of equilibrium all along the project showed some variation of mechanical properties: under the same control conditions (i.e. 8% - 175 °C - 30 seconds - 264 MPa - 50 bar/s), the average bending strength of specimens tested 2 weeks after production were 28.9 MPa in Table III – 6 during the pressure effect evaluation (III.2.G), 34.8 MPa in Table III – 9 during the moisture / temperature effect evaluation (III.3.C) consistent with the value of 35.9 MPa presented in Table II – 1 (2 months old specimens), and 43.3 MPa in Table III – 13 during this last ageing experiment. It is highly possible that the operator effect could explain this variability, and that is why a new reference was produced each time for comparison. The ageing of the specimens should also be run on a longer time period.

III.7 Discussion: about the structure / property relationship of compacted cellulose specimens

III.7.A The specimens' structure as a result of the compaction process

A laminated structure

Commercial α-cellulose is composed of cellulose fibers, which are hollow cylindroids of 10-30 µm of external diameter and a wall thickness of 3 – 5 µm. The length differs from one lot to another; the α-cellulose lot used in this thesis had particles with length from 100µm to 500 µm, and sometimes more, up to 1 mm (Figure III - 26).

Figure III - 26: SEM picture of α-cellulose powder

On the fracture of specimens after bending tests, a laminated structure was observed: sheets of about 300-500 µm wide are aligned perpendicular to the molding pressure, their thickness was evaluated using a digital caliper.

Figure III - 27: Piles of 6 halves of broken specimens in bending (left) and tensile (right)

The tensile specimens also showed a layered organization, but the sheets were a bit less obvious than those resulting from a bending failure (Figure III - 27). On the SEM pictures, without preparation of the samples, the laminated structure and the sheet-orientation of the fibers were confirmed (Figure III - 28).

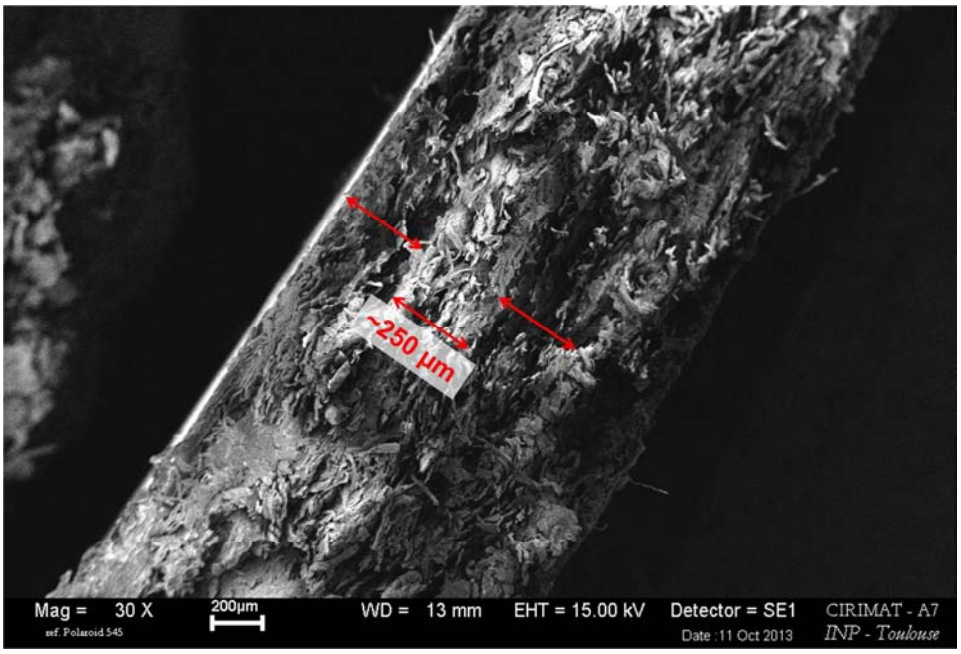


Figure III - 28: Cross sectional SEM picture of a broken control α-cellulose sample (in bending)

At first, it was not certain whether the sheets already exist in the material or were created as a result of the mechanical tests. Yet, the laminated structure appeared in tensile, in bending, and in bending performed in the other direction (with the small side up – Table III - 14). In the field of intertwined materials, the orthotropy resulting from the molding of fibers is a classic. It is also very unlikely that the same structural effect would be resulting from breakage of the material in the two directions of tensile / bending, the laminated structure thus results from the organization of the material itself which can be said orthotropic.

However, every attempt to perform observations on clean cross sections failed in retrieving the laminated structure. Upon sanding paper grinding, stone abrasion, microtone cutting, liquid nitrogen breaking, the inner structure of the specimens always appeared continuous, composed of particles (cross sections of compacted fibers - Figure III - 29) but the 300 microns sheets that should appear as a repeated pattern was never observed. A procedure for what was thought to be the best sample preparation is described in Figure III - 30. The wedge-shape was first given with grinding on 180 grit sandpaper (P180 ISO standards), and successfully passed on 360, 600 and finally 1200 grit sandpaper for a fine finish.

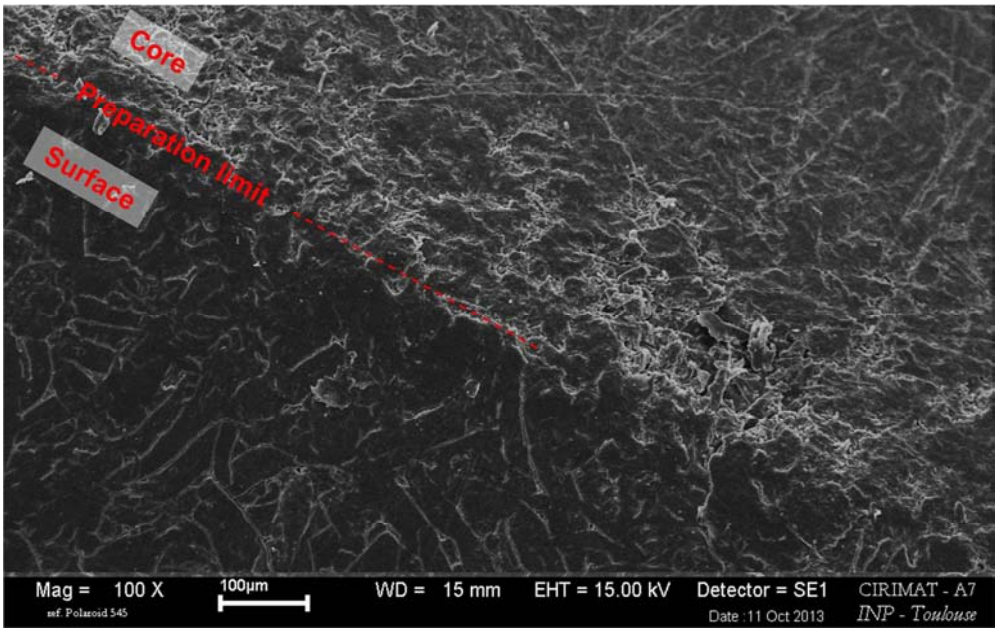


Figure III - 29: SEM picture of a surface and cross section of a sample after sandpaper preparation (180 – 360 – 600 – 1200 ISO grit)

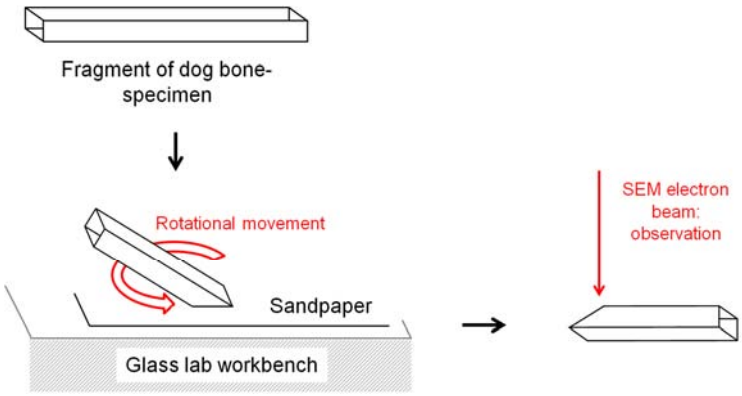


Figure III - 30: Sandpaper preparation for cross section observations

A marked surface effect

All along this work, bending properties have always been higher than tensile properties (Table III - 10 for instance). Normally, homogeneous materials should have tensile properties higher than bending properties, but, in the case of compacted cellulose, the orthotropic character (i.e. layered structure in the direction of bending) partially explains this behavior.

It was rapidly stated that the smoothness of the surface differed totally from the roughness of the inside of a specimen. After a breakage, the grinding and polishing of the inner structure did not produce anything comparable to the surface. Also, during the evaluation of the effect of specimens' thickness on the mechanical properties (III.2.B), it was detected (statistically significant, Pintiaux et al. 2013) that the tensile modulus was increased upon increase of the skin/core ratio (Figure III - 12). 3-points-bending is very impacted by the surface of a specimen because of the deformation pattern occurring during bending, whereas tensile deformation tests the specimen quite homogeneously among its cross-section (Figure III - 31).

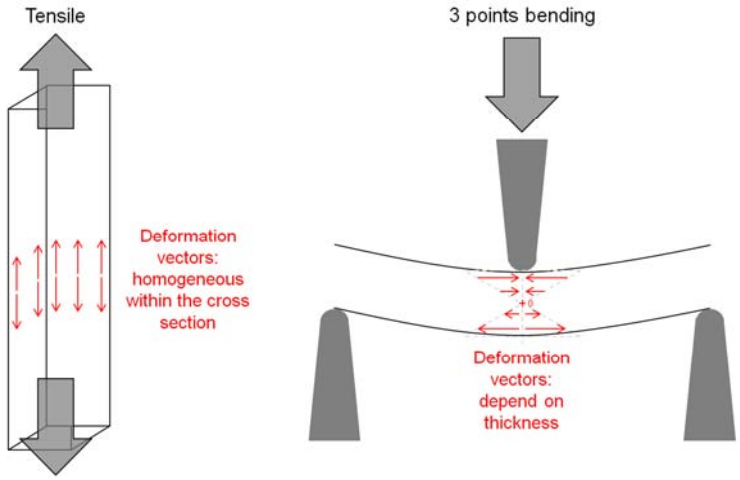


Figure III - 31: Deformation vectors in the case of tensile and 3 points bending

The compacted cellulose material was thus being considered, as a first simple approach, like a "sandwich structure", consisting of 3 layers (skin – core – skin). In this model, the tensile modulus of the skin was confirmed to be higher than the core, although the skin's density was equivalent to that of the core (Table III - 3). Later, it appeared that the lateral sides of the molded object were much more dense and thick than the up and down sides (in contact to the mold), which would complicate the model.

Nevertheless, the "sandwich model" with a stronger skin explains the higher bending properties observed all along this work. It also provides explanations about the higher response in bending to the variations of operating conditions: the skin, in contact of the mold is more rapidly at the mold temperature, moisture changes can occur more rapidly, and in contact of the mold, the pressure is more directly applied than in the core.

Manuel Marcus from the IMFT (Fluids Mechanics Institute of Toulouse) offered the opportunity to perform X-ray 3D tomography on some materials in order to evaluate structural differences at the skin. After scanning the specimens on the sides, the 3D image was reconstructed which permitted to visualize the porosity in the direction of the fibers. Generally, a higher porosity was detected in the core of the specimens. The pattern of porosity distribution showed that the faces in contact of the punches (perpendicular to the pressure) were only a few µm thick. The opposite surfaces in contact of the die were much thicker at about 300 µm thick which was quite surprising. On the following pictures, a color scale was applied to the porosity, high porosity appeared in deep blue medium porosity in light blue / grey, and orange – red was used for lower porosity zones. The same absolute scale was applied on all 4 specimens tested, in order to allow significant comparisons.

On the cross section of 8% cellulose pressed at room temperature (25°C – line T0 in Table III - 3), a large zone of high porosity (deep blue) can be observed in the core of the specimen compared to the other (Figure III - 32). The specific gravity of the specimen was measured at 1.481 g/cm^3 and was the lowest of Table III - 3. These specimens also had an equilibrium moisture content of 8.57 % which was even higher than the original powder (8.0 %).

In comparison, the specimen molded at 150°C from dry cellulose (0% MC powder – line M1 in Table III - 3) had a reduced low density zone, and a wider high density zones on the sides of the specimen (Figure III - 33). Extreme densities (red) were even observed on the lateral sides, and the up and down sides had a thicker high density area. The specific gravity measured on these specimens was consistently higher (1.489 g/cm^3) than the cold pressed specimens and their equilibrium moisture content also lower (7.62 %). However, the comparison of the mechanical properties of these specimens is surprising: the cold pressed, lower density, higher equilibrium MC specimens (8% – 25 °C) had better properties than the

specimens pressed at 0% 150°C (Table III – 3) which confirmed that density / porosity is not sufficient to explain the mechanical properties of the specimens (Cf III.2.G Effect of pressure).

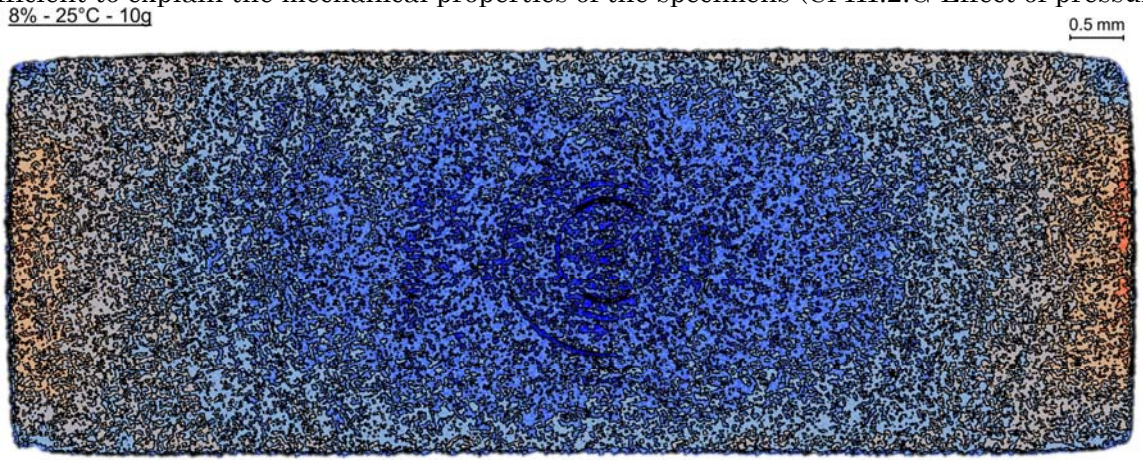


Figure III - 32: Cross section of compacted cellulose specimen at 8% - 25°C obtained in X ray tomography with a coloured blue – red porosity scale

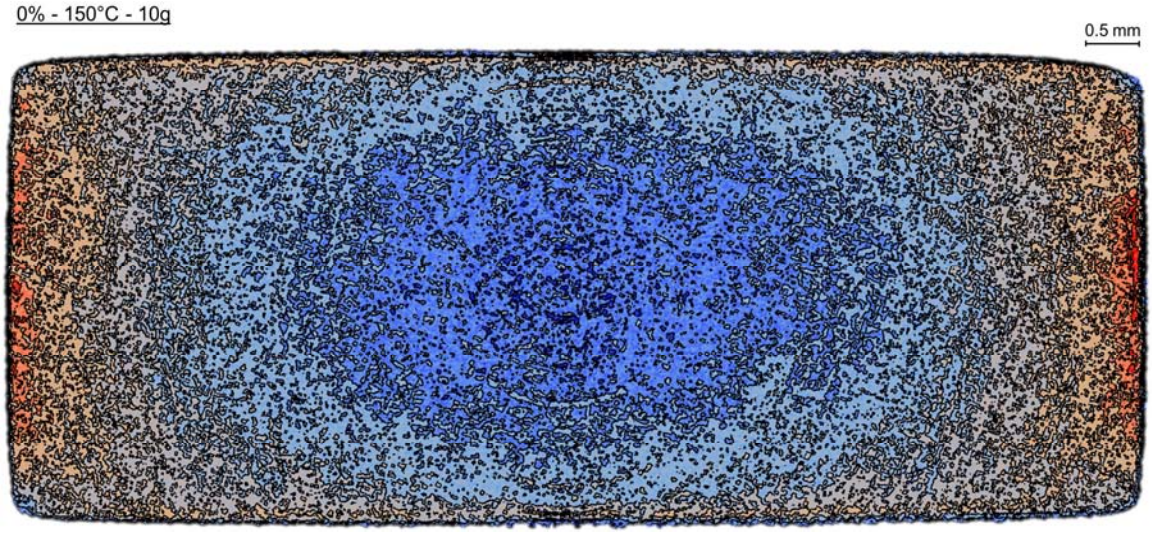


Figure III - 33: Cross section of compacted cellulose specimen at 0% - 150°C obtained in X ray tomography with a coloured blue – red porosity scale

Consistently strange results were obtained on X-ray tomography cross sections of 8% - 175°C and 2% - 250°C specimens: although the later had much higher mechanical properties than the former. The comparison of the porosity pattern showed that the low density zone in the core of 8% - 175°C (Figure III - 35) was smaller than 2% - 250°C (Figure III - 34). The 8% - 175°C (reference specimens) had an average density zone (grey / light blue) that appeared larger and much more continuous than the 2% - 250°C. The sides, however were about the same proportion between the two conditions, but significantly higher density was observed on the 2% - 250°C specimen.

Despite its extraordinary mechanical performances, the porosity pattern of the 2% - 250°C specimen was very similar to the 0% - 150°C (Figure III - 33) which had the lowest mechanical properties ever obtained during this PhD work.

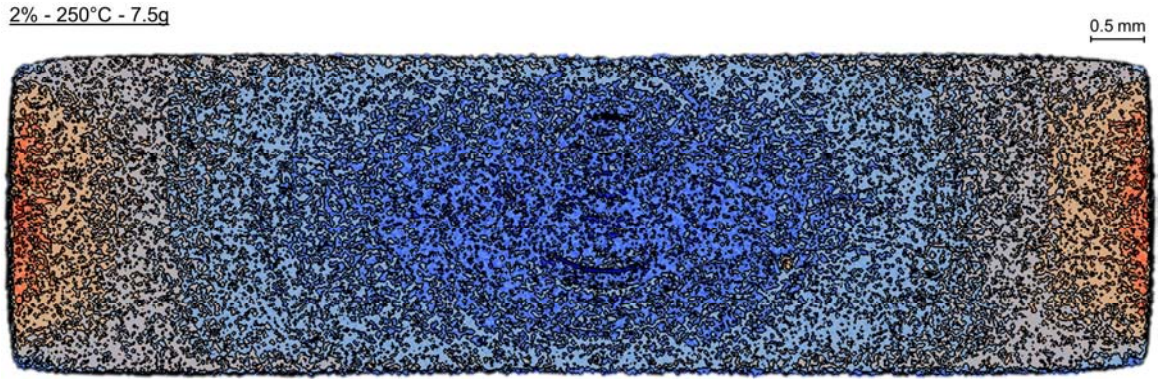


Figure III - 34: Cross section of compacted cellulose specimen at 2% - 250°C obtained in X ray tomography with a coloured blue – red porosity scale

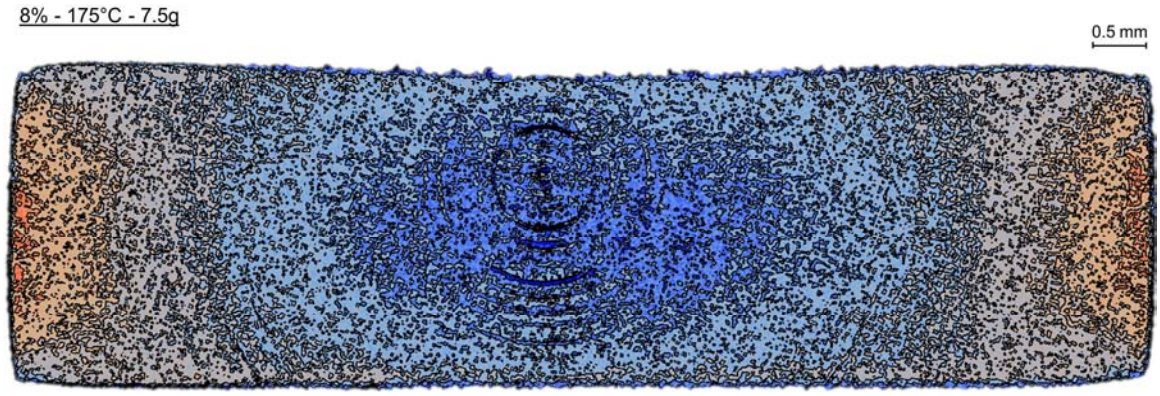


Figure III - 35: Cross section of compacted cellulose specimen at 8% - 175 °C obtained in X ray tomography with a coloured blue – red porosity scale

Following the discovery of the much higher thickness of the high density skin zone on the lateral (short) sides of the specimens compared to the up and down sides, bending tests were performed in the direction of the short side i.e. the specimen lying on its side on the 3 points bending setup. The bending properties were thus calculated, considering a thickness of 10 mm (long side) and a width of about 2.7 mm while testing the material on the short side.

Table III - 14: Bending tests performed in the two directions of the long side (classic) and short side

	Bending strength at break		Bending modulus	
	MPa		GPa	
	Mean	St dev	Mean	St dev
Long side (reference)	45.3	1.2	6.9	0.3
Short side	51.8	2.8	6.7	0.2

As seen on Table III - 14, a higher bending strength at break was obtained while testing the material in bending on the short side compared to the long side reference. On the other hand, the bending moduli were similar under the two conditions. This confirms the skin effect and its important role in the mechanical properties of the specimens and the fact it has to be considered in the explanation of the mechanisms of cohesion.

III.7.B Mechanisms of cohesion

The structural changes during compaction molding

The first step of compaction molding is the pre-compression of the powder, which consumes most of the porosity by expelling the air between the particles. This step requires very low pressure and does not produce any mechanical properties; pre-compressed powder does not possess sufficient cohesion to be held by hand.

During the second step, the particles get closer one to the others and friction occurs, which locally increases temperature, increases further the density but the deformation of the particles is not complete as the surface area (Table III - 15) is not much affected (Vaca-Medina et al. 2013). Studies performed by Laurent HEUX at the CERMAV in Grenoble showed that the material resulting from cold compression was much more amorphous than the original powder which precises the effect of pressure on the breaking and disordering of the crystallites. Consistently, cold pressed specimens had an equilibrium moisture content higher than the original powder (Table III – 3 and previous part III.7.1) which could be a result of its amorphization. The data provided by Vaca-medina did not observe this decrease of crystallinity which would much likely be due to the effect of crystal orientation on the X-ray diffraction measurements between the powder and a compacted sample (Figure III - 14).

Table III - 15: Properties of compressed cellulose samples (from Vaca-medina et al. 2013)

Cellulose sample	Crystallinity index[a]	BET		
		Surface area (m^2/g)	Sorption constant	R^2
Vitacel L600/30				
Powder	48 (4.2)	169	8.006	0.997
25 °C	59 (1.9)	163	7.159	0.999
160 °C	64 (2.5)	122	6.953	0.998
α-Cellulose				
Powder	62 (3.0)	136	9.136	0.998
25 °C	66 (3.1)	135	6.617	0.997
160 °C	73 (3.6)	124	7.639	0.998

The third step is characterized by the action of temperature, which begins, and takes place to a higher extent at the surface of the material, where the temperature is first increased and higher in the process. Jallabert (PhD thesis 2014) showed that during the compaction process, a transition temperature is crossed for what hypothesis was that it could be the glass transition temperature of cellulose (Figure III - 36). The decrease of surface area on the resulting material compared to the original powder and to the cold-compressed material (Table III - 15) supports this hypothesis: under the effect of temperature, the Tg is crossed and the fibers can be deformed and remain in this deformed state which facilitates the establishment of the hydrogen bonding network. In parallel, crystallinity studies made at the CERMAV have shown a much higher crystallinity at the skin than in the core of the hot-pressed samples which was consistent with the data of Vaca-medina et al. (Table III - 15).

The temperature effect is well described in this chapter as a drastic increase of the mechanical properties, which are directly impacted by the establishment of a hydrogen bonding network to a higher extent. Data available in this chapter (Table III - 3) have also shown an increase of density with molding temperature which can be explained by the higher deformability of the fibers because higher temperature allowed more material (not only the surface) to cross the Tg. An hypothesis was thus formulated: The effect of pressure

would be the amorphization of the cellulose, but then temperature allows to recrystallize some of this amorphized cellulose (co-crystallize), which brings higher mechanical properties, lower porosity, lower BET surface area. The recrystallization step could either take place during the molding, or during the cooldown of the sample.

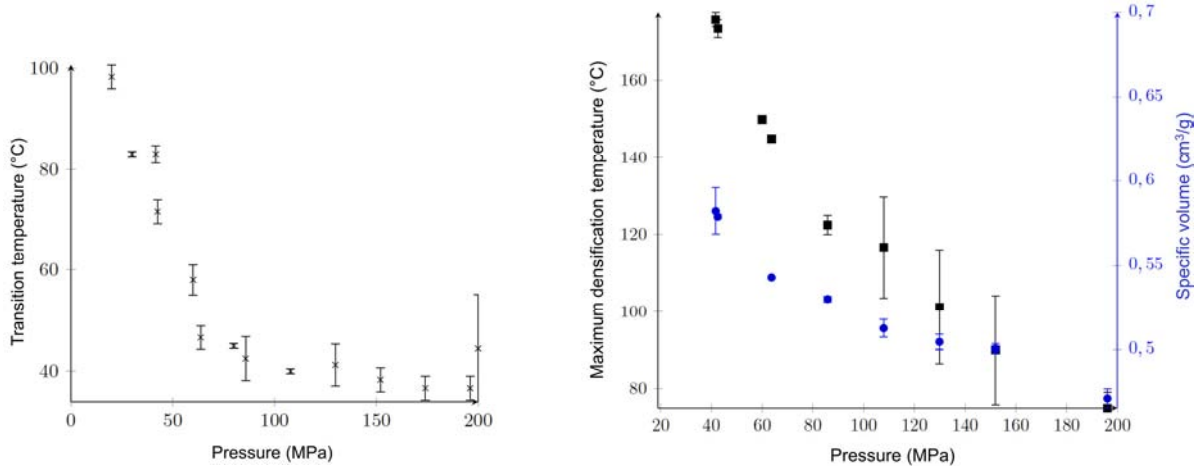


Figure III - 36: Transition temperature, maximum densification temperature and specific volume plotted against molding pressure (from Jallabert 2014 PhD thesis)

Surprisingly, the increase of the molding time was not observed to increase the mechanical properties (Table III – 3), although it should help to conduct the temperature inside the material and cross the Tg in the whole specimen. The X-ray tomography analysis in the previous part are consistent with this observation, as the porosity pattern are not directly correlated to the in a specimen does not change as much as its mechanical properties. Further anlysis would be needed to fully elucidate these statements.

The central role of water

The presence of some moisture was concluded to be necessary in the research of increased mechanical properties. Jallabert also confirmed that the densification step did not occur on dry compacted powder from 0 to 160°C (Figure III - 37).

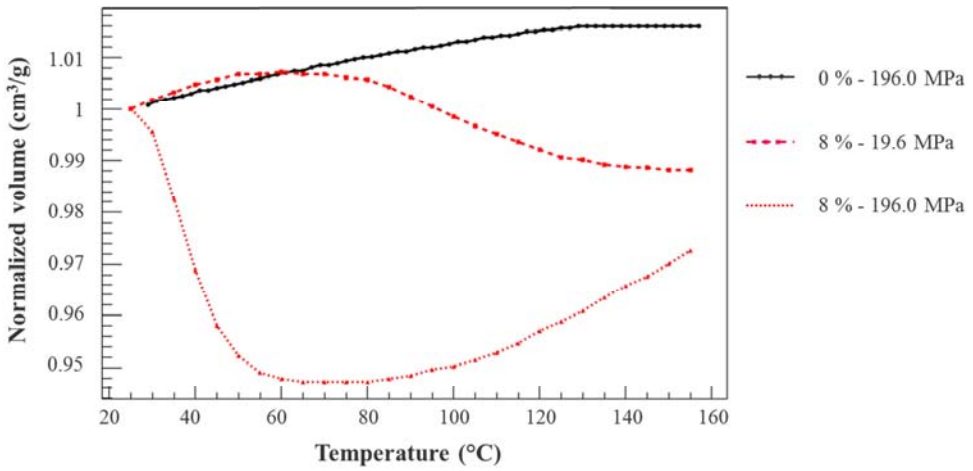


Figure III - 37: PVT diagrams for compacted α-cellulose (Jallabert PhD thesis 2014)

Plant lignocellulosic constituents' Tg depends on moisture (Chapter I). It is possible that Jallabert did not observe a densification because the Tg of dry cellulose (220°C) was not crossed in these conditions of temperature (i.e. up to 160°C). Consistently, the mechanical properties of dry cellulose brutally increased from 225°C (mold temperature) to 250°C (Table III - 9 and Table III - 10). More data would be needed to verify these statements.

The concomitant effect of temperature and moisture had been studied in regard to the mechanical properties in this chapter (III.3) and it was found that the best properties were obtained at 2% moisture which is below the monolayer of sorbed water for cellulose (5% see materials and methods VI.2.C). Jallabert during his PhD work also obtained the best specimens with gelatinized starch at 4% of MC, below the monolayer calculated at 9.7% (Jallabert, PhD thesis 2014).

The moisture / temperature effect is also responsible for a major drawback of compaction molding: delamination. When moisture is high (i.e. 8%) the increase of the temperature from 175 to 200°C leads to delamination. Upon increase of the temperature to 225 and 250 °C the delamination decreases. Yet, at 250°C and 8% MC, the mechanical properties are only slightly increased compared to the other moistures. Two main hypotheses can be formulated to explain the reduction of the delamination at increased temperature:

* Water could be consumed in hydrolysis reactions (Sasaki et al. 1998), which would reduce the steam pressure in the inner structure and explain the darkening of the specimens at higher temperatures.
* Water is not consumed and steam pressure increases but the strengthening of the skin due to high temperature permit to counteract the delamination effect and the higher strength of the specimens allows to prevent it from bursting. This hypothesis explains why the properties are only slightly increased at 250°C and 8% MC because the more water is in the material, the higher the steam pressure is, and thus the lower the core properties are.

About the steam pressure: most of these molding conditions put water into a subcritical state, which means that during the establishment of the hydrogen bonding, liquid (actually subcritical) water is accumulated in the inner part of the material and remains there which probably prevents the core's fibers from establishing hydrogen bonding because of this excess of water. It can be imagined that, in the inside of the material, liquid water is pushed by the pressure and temperature from the sides (because hydrogen bonding on the sides frees up water that follows the temperature gradient) and thus cellulose particles are "floating" in water which totally prevents contact and chances of hydrogen bonding. The group of Navard et al. studied the effect of pressure molding from 700 MPa to 2.5 GPa on the destructuration of cotton linters. One of their conclusions was that moist cotton linters were torn apart into 15 to 150 nm nanoelements at the surface only whereas dry cotton linters underwent this transformation in the whole specimens (Privas et al. 2013). In this case, moisture prevented the destructuration of the cotton linters in the core of the samples and the establishment of a hydrogen bonding network was thus hindered which is compatible with the hypothesis formulated here.

Thus, upon reduction of moisture, high temperature is necessary to remain over the Tg, which guarantees a strong skin capable of resisting to the steam pressure inside the material, but the reduction of moisture also reduces the steam pressure and lowers the overall quantity of water in the material which gives more chances to cellulose fibers to create cohesion. Moisture is reduced and the strength of the specimens is increasing until 2% (monolayer) which provides a strong skin and the least steam pressure (or no pressure?) which participate in higher cohesion in the core of the material. If more water is removed, the thermal conductivity is lowered, and even though at 250°C the Tg is crossed, the resulting skin is probably thinner or weaker as the temperature dependent cohesion mechanisms cannot take place in the inner part.

The double role of water can be summarized this way: water reduces the Tg which is crucial for deforming particles and thus creating a hydrogen bonding network, and it

increases the thermal conductivity which permits to build up stronger cohesion at the surface and deeper in the core of the material.

However, the X-ray tomography did not support these hypotheses, the skin of the strongest materials did not appear much thicker or with much higher density, at least not in the proportion of the properties' increase and the core of these specimens exhibited as much porosity as the others. From the data collected on the structure / property relationship during this thesis work, it can be concluded that the densification process is not sufficient in order to explain the mechanical properties. These explanations were not the primary objective of this thesis, thus only hypothesis have been formulated on incomplete data which nevertheless conducted to a solid basis for future research.

III.8 α-cellulose flowability investigation trials (Nagoya)

While trying to mold cellulose in 3D, certain flowability was observed (Figure II - 14). The idea of trying to measure to flow properties of cellulose arose with the internship in Nagoya, in the research team of Miki et al. that have already been working on measuring the flow properties of highly charged WPC composites (Imanishi et al. 2005a; Imanishi et al. 2005b).

The setup used in Nagoya was capable of 285 MPa in the chamber. Several dies were available, the first one to be tested was a 4 mm diameter and 10 mm length die. The abbreviation (4,10) is used in this part for dies' diameter and length. An average extrusion speed was set up for the first tests (10 mm/min). As the extrusion is working, the pressing machine automatically adapt the force needed to maintain the flow rate, this force is recorded. If the force exceeds the capacity of the press, the experiment stops.

Cellulose equilibrated with reference climatic conditions (25°C – 60% RH) did not flow at 150°C. The temperature was increased to 200°C, and it did not flow either. In order to increase the flowability, cellulose was let to equilibrate in a high moisture environment (50°C – 100% RH) which produced a MC of 13.66 ± 0.43 %. Another trial was made, and it did not flow. At this time, the powder was charged directly in the hot chamber, with possibility of losing moisture during the charging time thus it was decided to pre-mold cylinders (28 mm diameter) in a cold chamber, letting the pre-compressed plots a few days more to equilibrate, and another trial was performed using these pre-compressed plots as starting material which permitted to charge the mold and start the experiment in only a few seconds. This last trial was a success, a flow occurred and a force - displacement curve was recorded. The experiments were pursued using dies (4,20), (3,10), (2,10) and (5,10). Force displacement curves for these experiments were drawn together in Figure III - 38.

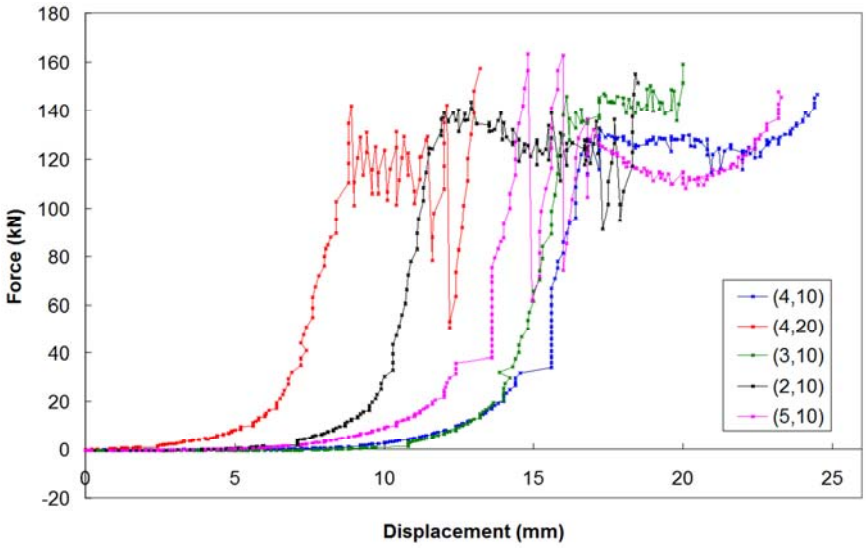


Figure III - 38: Force-displacement curves for moistened cellulose flow tests at 200°C in Nagoya

The (2,10) and the (4,20) had an extremely erratic behavior, with no stabilization of the extrusion force. During the experiment, the material was ejected through the die with violent vibration and sound of explosion and spread all around the press. The hypothesis was formulated that steam accumulation could have produced this explosive extrusion. The (4,10) and the (3,10) curves were almost usable as a plateau was present at the end of the experiment for which a relatively stable extrusion force of 128 and 142 kN were recorded. The (5,10) experiment started with explosions and finally extrusion begun but the flow did not reach a stabilized state.

The results of the flow experiment were collected and are presented in Figure III - 39. Even if most of the extrusion took place at a relatively stable force, the extrudate formed small pellets of cellulose that reminds the shark-skin aspect of highly charged extruded WPC composites.

Figure III - 39: Extruded moistened cellulose off the (4,10) at 200°C (on the left), 100°C on the right

The explosive extrusion on dies (2,10) and (4,20) occurred because of the stick slip phenomenon. The possibility of having steam accumulating, suddenly released at the exit of the die and pushing the material out was formulated. It was thus decided to perform the tests at 100°C (Figure III - 40).

The stick slip phenomenon did not occur at 100°C as much as it did at 200°C but the extrusion force was still unstable and the desired values were not obtained. The extruded product had a quite different aspect compared to the previous tests at 200°C (Figure III - 39).

Because of the impossibility of measuring a stabilized force during extrusion on several dies, another possibility was to study a fewer number of dies but different extrusion speeds. First trials were made on the (4,10) die, and extrusion speeds of 1.5, 10, 20 and 50 mm/min were tested (Figure III - 41) but again, the data were not usable.

Magnesium stearate (10%) which is a classic powder lubricant for the pharmaceutical industry, was evaluated in order to correct the poor flowability of cellulose. The magnesium stearate addition produced even worse curves than pure cellulose (data not shown), these measurements were finally abandoned.

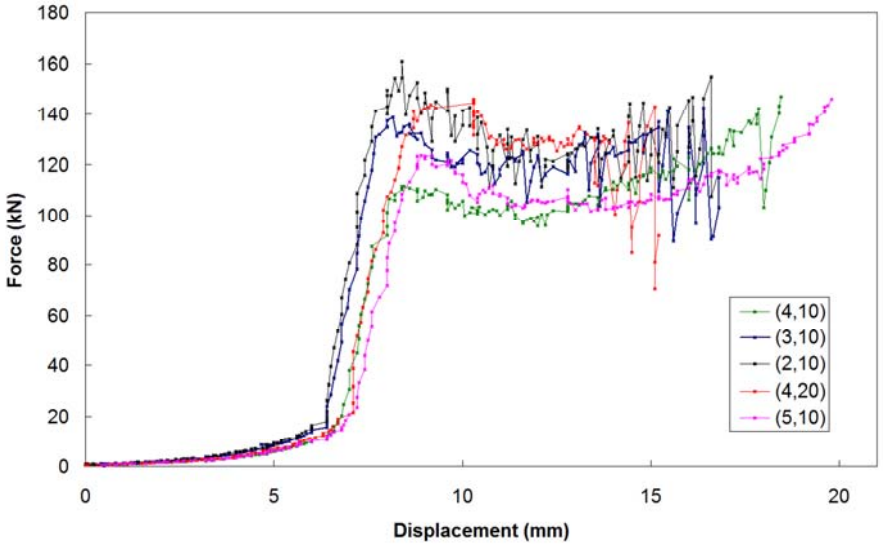


Figure III - 40: Force-displacement curves for moistened cellulose flow tests at 100°C in Nagoya

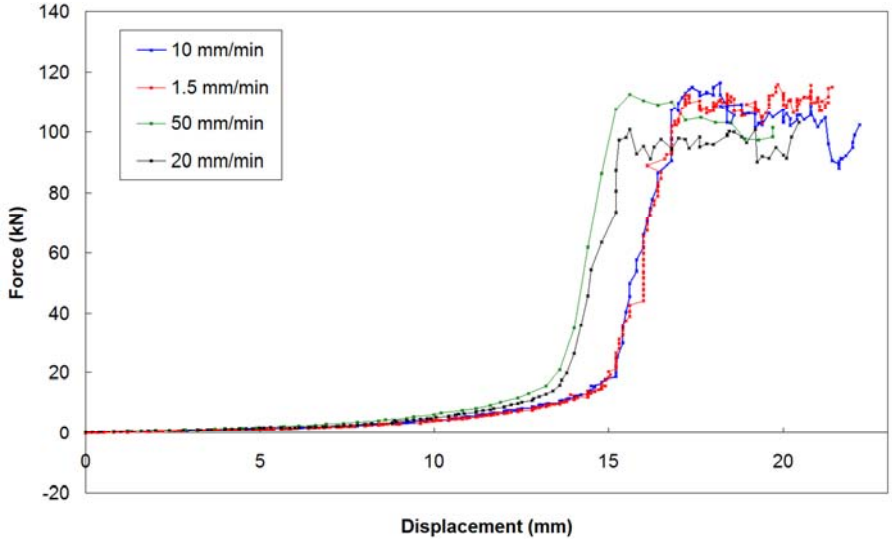


Figure III - 41: Force-displacement curves for moistened cellulose flow tests at 100°C through a (4,10) die in Nagoya

Conclusions

1. The effect of the molding parameters was first studied independently one from the others. The molding time (studied from 3 to 300 seconds) was seen to have no effect on the mechanical properties but specimens molded for a longer time tended to have a lower equilibrium moisture content and a higher density. The increase of pressurization speed was observed to produce higher mechanical properties. These two parameters were not further examined and had the least effect of all. Thus, their values were set to respectively 30 seconds and 50 bar/s (maximum) for the rest of the chapter. The effect of mass variation was studied, and although the bending properties and the tensile strength were not affected, the tensile modulus was drastically increased upon mass reduction. This revealed the existence of different layers in the material, a weaker core and a skin with a higher modulus i.e. less deformability. The density and equilibrium moisture content measurements performed did not permit to detect structural differences between the core and the skin. A reference was established at 7.5 g (i.e. specimens of ~2.7 mm thick). The effect of moisture was first studied at 0 - 6 - 8 and 10%, by drying and equilibrating cellulose to relative humidities of 45, 60 and 75 %. Dry specimens had the lowest mechanical properties, low density and high equilibrium moisture content. Slightly lower mechanical properties were obtained for the highest moisture but less difference was observed between the two other conditions. The effect of pressure was studied although this work was based on high pressure molding and less effect was observed after 100 MPa. It appeared that the specific mechanical properties followed a logarithmic curve, which concluded that higher mechanical properties were not only an effect of higher density. The effect of temperature was first studied at 25°C, and from 100 to 200°C. Temperature increased all the mechanical properties, the specimens' density and reduced the equilibrium moisture content and the interparticular voids, linearly until 200°C, temperature which triggered the delamination of the samples. Temperature was definitely the most impacting parameter.

2. Some additional data related to the properties of compacted cellulose samples were also provided: water tests were conducted on reference samples which showed that the swelling and adsorption were important, but less than expected. The mechanical properties of moist specimens were also performed which confirmed the water sensitivity of the cellulose specimens. All along this thesis work, reference samples have been produced and although being produced in the same operating conditions, exhibited slightly different mechanical results. The ageing of the specimens was performed and did not provide a satisfactory explanation to the observed variation, which thus resulted from other poorly controlled parameters (for instance operator effects like manual filling of the mold).

3. As delamination resulted from steam pressure in the inner layers of the material, built up at high temperature, these two parameters (moisture and temperature) were deeper investigated. The effect of moisture reduction (8 to 0 %) and increase of temperature (175 to 250 °C) were studied together, in order to understand the conditions that triggered delamination and measure the evolution of the mechanical properties. Delamination occurred around the 8% - 200°C point but only slightly at 6% - 200°C and 8% -225°C. 2% of moisture produced specimens with by far the best mechanical properties. The further increase of the temperature consistently increased the mechanical properties, as well as initiated a colour change on the specimens. 250°C specimens were by far the strongest specimens produced within this thesis work. When moisture was further reduced (0%) the mechanical properties were decreased but not as much as previously stated because mostly of the higher temperature employed.

4. These results, together with those obtained by Jallabert during his PhD thesis and the works of Vaca-medina et al. permitted to formulate hypotheses concerning the structure / property relationship. The compacted cellulose material was heterogeneous orthotropic because of the orientation of the fibers perpendicular to the molding pressure. The skin effect

detected while evaluating the effect of mass changes together with the orthotropy of the material provided an explanation for the higher properties measured in bending than in tensile and the hypothesis of a "sandwich model" was proposed. X ray tomography analyses permitted to visualize the porosity distribution along the cross section of some samples. It was revealed that the long side faces (orthogonal to the pressure axis) in contact to the punches were much less dense and thick than the short sides (parallel to the pressure axis) in contact to the die of the mold. The difference of density / thickness of the skin on parallel / orthogonal sides was only slightly correlated to higher properties when testing the material in bending on the parallel sides. Also, poor correlation was established between the specimens' mechanical performances and the porosity distribution within their cross section. This, together with the results obtained upon the evaluation of the effect of pressure led to the conclusion that density / porosity patterns were not sufficient to explain the mechanical properties and the mechanisms of cohesion. Additional data were provided by crystallinity changes: the skin and core of cold-pressed and the core of hot-pressed specimens were more amorphous than the original cellulose powder and the skin of hot-pressed specimens had a crystallinity index comparable to that of the powder. All these elements permitted to formulate hypotheses concerning the mechanisms of cohesion: The high pressure constraint has a destructuring effect on cellulose which reduces crystallinity, increases the equilibrium moisture content of the samples compared to the powder and does not affect the BET surface area. Temperature and moisture are important to give molecular motion to the cellulose chains (glass transition) which provides better particles deformation, thus better contact between the particles, and, at a molecular scale the establishment of a solid hydrogen bonding network, followed by possible recrystallization / co-crystallisation phenomenon. Higher temperature and a minimum moisture are necessary to cross the Tg but also to develop the hydrogen bonding network between adjacent particles. The temperature / moisture couple also has a negative effect called delamination. There are thus two contradictory effects of moisture: a beneficial effect that is conducting heat from the skin to the core of the material and bringing additional molecular motion (lower Tg), and a negative effect that is the accumulation of free water in the core layers which prevents the establishment of the hydrogen bonding network and builds up steam pressure which leads to the delamination of the samples. The mechanical properties observed would thus be the results of the balance between cohesion at the skin and steam pressure in the core layers for which an optimum probably exist around 2% moisture.

5. Finally, the flowability of α-cellulose was studied during an internship in Japan in a research team who specialized in the study of flowability of bulk wood and resin-impregnated wood, and there was no way to make the cellulose flow under the reference conditions of moisture (equilibrium with 60% RH). The increase of MC allowed to obtain data but they were not exploitable for calculation. These experiments confirmed that the problem of the flowability of such non melting polymers is a difficult issue that would require much more investment and high technology and thus no data concerning 3D-molding were presented in this thesis work.

Lire
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de la thèse